(54) Title: LIQUID INKS USING A COVALENTLY CROSSLINKED GEL ORGANOSOL

(57) Abstract: Gel organosols dispersions, and high solids color inks based upon these dispersions, featuring a carrier liquid having a Kauri-Butanol number less than 30 and a covalently crosslinked copolymeric steric stabilizer covalently bonded to a thermoplastic (co)polymeric core that is insoluble in the carrier liquid. The steric stabilizer comprises the reaction product of a monomer mixture comprising no greater than 2 % by weight of a crosslinking monomer having a functionality of two or more.

LIQUID INKS USING A COVALENTLY CROSSLINKED GEL ORGANOSOL

TECHNICAL FIELD

This invention relates to liquid ink compositions, in particular, to pigments dispersed in crosslinked gel organosols to provide improved ink compositions and liquid toners for use in ink transfer, ionographic, electrographic and

7   electrophotographic printing processes.

BACKGROUND

Liquid inks are widely used in a variety of printing processes, for example offset, intaglio, rotogravure, ink jet and electrographic printing. Many of the desired characteristics of the pigment dispersions used in the liquid inks are the same for each of the respective processes even though the final ink formulations may be substantially different. For example, the stability of the pigment dispersion both on

14   the shelf and under shear conditions is an important consideration regardless of the final use of the liquid ink. The art continuously searches for more stable pigment dispersions to provide more flexibility in ink formulations which in turn yields better efficiency and waste reduction in the various printing processes.

Electrographic printing refers to a printing process that uses an applied electric field and charged particles to produce a printed image on a receptor material. The art generally refers to the charged particles as toners. Electrographic printing generally

21   includes electrostatographic printing, ionographic printing, electrophotographic printing and the like. In electrophotographic applications, which include devices such as photocopiers, laser printers, facsimile machines and the like, the toners may be in the form of dry particles or particles dispersed in a carrier liquid. Particles dispersed in a liquid medium for imaging purposes are generally referred to as liquid inks, liquid toners or liquid developers.

Generally, the electrophotographic process includes the steps of forming a

28   latent electrostatic image on a charged photoconductor by exposing the photoconductor to radiation in an imagewise pattern, developing the image by contacting the photoconductor with a liquid developer, and finally transferring the

image t a receptor. The final transfer step may be performed either directly or indirectly through an intermediate transport member. The developed image is usually subjected to heat and/or pressure to permanently fuse the image to the receptor.

In the field of electrographic printing, particularly electrophotographic printing, a variety of both liquid and dry developing compositions have been employed to develop the latent electrostatic images. Dry toner compositions suffer

7   from a number of disadvantages. For example, dry toners are known to be difficult to control during the latent image development and transfer processes; this leads to toner scatter within the printer device and may create excessive amounts of dust and abrasive wear of the printer components. Some dry toner compositions must also be fixed by fusing at elevated temperature, which requires a large source of energy and may limit the choices of receptor materials to which the developed latent image may be transferred. Moreover, dry toners must be triboelectrically charged, which makes

14   the printing process very sensitive to both the temperature and humidity of the ambient air and may result in printing delays due to charge equilibration. The limited particle size of the toner is another disadvantage of dry toners. If the particle size is small, the dry toner can become airborne and create a potential health hazard due to inhalation of the particles. On the other hand, the larger particle sizes make it difficult to obtain high resolution images.

Many of the disadvantages accompanying the use of dry toner compositions

21   have been avoided by the use of liquid developers or toners. For example, liquid toners contain smaller particles than dry toners resulting in higher resolution images. In addition, liquid toners are not triboelectrically charged; therefore, they are much less sensitive to changes in ambient temperature and humidity. Since the toner particles in a liquid developer are contained within a fluid phase, toner scatter and dust accumulation do not occur within the printer. In addition, the particles being contained within a liquid matrix will not become airborne thus eliminating the risk of

28   inhalation of the particles.

Liquid toners typically comprise an electrically insulating liquid that serves as a carrier for a dispersion of charged particles known as toner particles composed of a colorant and a polymeric binder. A charge control agent is often included as a component of the liquid developer in order to regulate the polarity and magnitude of

2

the charge on the toner particles. Liquid toners can be categ rized into two primary classes, for convenience, the two classes will be referred to as conventi nal liquid toners and organosol toners.

Of particular utility are the class of liquid toners which make use of self-stable graft copolymers dispersed in an organic solvent (organosols) as polymeric binders to promote self-fixing of a developed latent image. U.S. Patent Nos. 3,753,760;
7   3,900,412; 3,991,226; 4,476,210; 4,789,616; 4,728,983; 4,925,766; 4,946,753; 4,978,598 and 4,988,602 describe compositions and uses of graft copolymer organosols. Exemplary liquid electrophotographic, pigmented inks made using self-stable graft copolymer organosols are illustrated by Kosel in U.S. 3,900,412.

Self-stable organosols are colloidal (0.1-1 micron diameter) particles of polymeric binder which are typically synthesized by nonaqueous dispersion polymerization in a low dielectric hydrocarbon solvent. These organosol particles are
14   sterically-stabilized with respect to aggregation by the use of a physically-adsorbed or chemically-grafted soluble polymer. Details of the mechanism of such steric stabilization are provided in Napper, D.H., Polymeric Stabilization of Colloidal Dispersions, Academic Press, New York, NY, 1983. Procedures for effecting the synthesis of self-stable organosols are known to those skilled in the art and are described in Dispersion Polymerization in Organic Media, K.E. J. Barrett, ed., John Wiley: New York, NY, 1975. Although it is generally recognized that the solvation
21   of the particle is critical in the formation of a dispersion, none of the foregoing references recognizes the utility of a gel in forming a stable dispersion.

The most commonly used non-aqueous dispersion polymerization method is a free radical polymerization carried out when one or more ethylenically-unsaturated (typically acrylic) monomers, soluble in a hydrocarbon medium, are polymerized in the presence of a preformed amphipathic polymer. The preformed amphipathic polymer, commonly referred to as the stabilizer, has two distinct ends, one essentially
28   insoluble in the hydrocarbon medium, the other freely soluble. When the polymerization proceeds to a fractional conversion of monomer corresponding to a critical molecular weight, the solubility limit is exceeded and the polymer precipitates from solution, forming a core particle. The amphipathic polymer then either adsorbs onto or covalently bonds to the core, which core continues to grow as a discrete

3

particle. The particles continue to grow until monomer is depleted; the adsorbed amphipathic polymer "shell" acts to sterically-stabilize the growing core particles with respect to aggregation. The resulting core/shell polymer particles comprise a self-stable, nonaqueous colloidal dispersion (organosol) comprised of distinct spherical particles in the size (diameter) range 0.1-0.5 microns.

The resulting organosols can be subsequently converted to liquid toners by simple incorporation of the colorant (pigment) and charge director, followed by high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling or other means known in the art for effecting particle size reduction in a dispersion. The input of mechanical energy to the dispersion during milling acts to break down aggregated pigment particles into primary particles (0.05-1.0 micron diameter) and to "shred" the organosol into fragments which adhere to the newly-created pigment surface, thereby acting to sterically-stabilize the pigment particles with respect to aggregation. The charge director may physically or chemically adsorb onto the pigment, the organosol or both. The result is a sterically-stabilized, charged, nonaqueous pigment dispersion in the size range 0.1-2.0 microns, with typical toner particle diameters between 0.1-0.5 microns. Such a sterically-stabilized dispersion is ideally suited for use in high resolution printing.

Rapid self-fixing is a critical requirement for liquid toner performance to avoid printing defects (such a smearing or trailing-edge tailing) and incomplete transfer in high speed printing. A description of these types of defects and methods of preventing them using film forming compositions are described in U.S. Patent Nos. 5,302,482; 5,061,583; 4,925,766; 4,507,377; and 4,480,022.

Another important consideration in formulating a liquid toner is the tack of the image on the final receptor. If the image has a residual tack, then the image may become embossed or picked off when placed in contact with another surface. This is especially a problem when printed sheets are placed in a stack. If the image is tacky, it may transfer to the backside of the adjacent sheet. To address this concern, a film laminate or protective layer is typically placed over the surface of the image. This adds both extra cost of materials and extra process steps to apply the protective layer.

It is further known in the art that film-f rming liquid toners fabricated using self-stable organosols generally exhibit excellent aggregation stability; however, the sedimentation stability of such inks is poor. Once the components of an organosol ink have settled, they are generally difficult if not impossible to redisperse to a degree of dispersion equivalent to the original, unsettled ink. This situation arises because self-stable organosol inks settle into closely packed, dilatant sediments, and irreversible

7   film formation can occur in these sediments when the volume fraction of organosol in the sediment exceeds the critical volume fraction required for film formation to occur (generally greater than 70 volume percent organosol). Hence, there is a need for liquid ink compositions that will overcome this poor sedimentation and redispersion behavior of organosol inks.

Attempts have been made to provide liquid developers having improved storage and thermal stability using a two component gel/latex system. U.S. Patent

14   Nos. 4,374,918; 4,363,863; 4,306,009; GB 2,066,493; and GB 2,065,320 describe liquid developers incorporating polymers having borderline solubility in the carrier solvent. A weakly crosslinked stabilizing gel and a separate latex (or gelatex) are used as a dispersant and/or fixative. The gel and latex are separate molecular species in the ink formulation. That is, the weakly crosslinked gel and latex are not covalently bonded to each other. Separate molecular components can lead to preferential depletion of one of the two components during extended printing thus

21   adversely effecting print quality. Separate components can also result in a broad molecular weight distribution for stabilizing the gel, which may have an adverse affect on the toner charge characteristics. In addition, the separate materials may lead to high free phase conductivity.

Recent attempts have also been made to overcome the poor sedimentation stability of pigmented liquid toners by replacing the pigment with a dye of significantly lower density. U.S. 4,816,370 describes liquid developers using a

28   thermally reversible, flocculated, dyed organosol. U.S. 4,476,210 and 4,762,764 similarly describe liquid developers using self-stable dyed organosols. The colorants used in each of these references are dyes rather than pigments. It is well established in the art that dyes are less stable to light and have a tendency to migrate (bleed) or sublime. Even though dyes have inherent advantages, such as transparency of the

colors and less interference with the characteristics of the thermoplastic binders, their poor light stability often times overrides these advantages. Moreover, becaus f the typically low mass of dye molecules relative to pigments, the charge/mass of dyed toners is generally higher by an order of magnitude than pigmented toners; this can lead to problems in printing dye-based inks to adequate optical density using liquid electrographic development processes.

7   More recent attempts to address the poor sedimentation and redispersion behavior of pigmented organosol inks are described in U.S. 5,698,616 and U.S. 5,652,282. These patents describe liquid inks that make use of a gel organosol to improve the sedimentation and redispersion properties of pigmented inks. The gel organosols disclosed in these patents are graft copolymers dispersed in an aliphatic hydrocarbon carrier solvent. The gel organosols, comprising graft copolymers in which a high molecular weight polymeric steric stabilizer (graft stabilizer) is

14   covalently bonded to an insoluble, high molecular weight thermoplastic polymeric core, have the ability to form a three dimensional network of controlled rigidity. The gels are formed by manipulating the solubility parameter difference between the graft stabilizer and the carrier solvent to a range of 2.5-3.0 $MPa^{1/2}$. The gel structures were found to improve liquid ink performance, particularly pigmented liquid electrographic/electrophotographic ink performance, by increasing the sedimentation stability and redispersability of the colorants without compromising print quality,

21   charge stability, or ink transfer performance.

Another issue relating to images printed using liquid inks is image durability. Durability refers to the resistance of the printed images to damage by blocking when printed sheets are stacked, erasure resistance, scratch resistance and abrasion resistance. Generally, images printed with liquid toners are less durable than images printed using dry toners. The lower durability of liquid ink printed images may result from a variety of reasons known to those skilled in the art. These include the

28   relatively lower thickness of printed ink films made using liquid toners, the relatively lower adhesive strength of some liquid toners to their print receptors, and the relatively lower cohesive strength of some printed liquid toners due to the comparatively lower glass transition temperature of the polymeric binders used in these liquid inks.

Various methods have been proposed to improve the durability of printed images made using liquid toners. In particular, U.S. 5,886,067 describes improved durability liquid inks comprising a controlled crystallinity organosol that is not a gel organosol. The controlled crystallinity organosol comprises an insoluble core and a soluble graft stabilizer prepared from a side-chain or main chain crystallizing polymeric moiety that independently and reversibly crystallizes at or above 22°C.

7   Such controlled crystallinity organosols impart improved blocking resistance, erasure resistance, and abrasion resistance to liquid inks containing the organosol. Suitable crystallizing polymeric moieties for incorporation into a graft stabilizer include >C_{14} acrylic and methacrylic esters, which do not form gel organosols based upon solubility parameter difference between graft stabilizer and carrier solvent.

SUMMARY OF THE INVENTION

In one aspect, the invention features a rapidly self-fixing ink with improved

14   sedimentation and redispersion characteristics useful as a liquid toner in ionographic or electrographic (electrophotographic or electrostatic) imaging and printing processes. The ink is comprised of a polymeric binder in the form of a graft copolymer gel, formed by intermolecular crosslinking, dispersed in an organic solvent or solvent blend having a Kauri-Butanol (KB) number less than 30, and optionally contains one or more colorants. The colorants may take the form of dyes or pigments. One or more charge controlling additives may optionally be added to the ink

21   formulation.

"Kauri-Butanol" refers to an ASTM Test Method D1133-54T. The Kauri-Butanol Number (KB) is a measure of the tolerance of a standard solution of kauri resin in 1-butanol to an added hydrocarbon diluent and is measured as the volume in milliliters (mL) at 25°C of the solvent required to produce a certain defined degree of turbidity when added to 20 g of a standard kauri-1-butanol solution. Standard values are toluene (KB = 105) and 75% by volume of heptane with 25% by volume toluene

28   (KB = 40). There is an approximately linear relationship between the Hildebrand solubility parameter and the KB number for hydrocarbons: Hildebrand Solubility Parameter $(MPa^{1/2}) = 2.0455[6.3 + 0.03KB \ (mL)]$.

The graft copolymer is comprised of a soluble or marginally insoluble high molecular weight (co)polymeric steric stabilizer ("graft stabilizer") covalently bonded to an insoluble, high molecular weight thermoplastic (co)polymeric backbone ("organosol core"). The gel is formed by incorporating a low percentage (typically less than 1.6% w/w) of monomer having a functionality $\chi 2$ in the graft stabilizer, and crosslinking the graft stabilizer to form intermolecular covalent bonds. The

7   crosslinked graft stabilizer, when further polymerized in the presence of core monomers, forms graft copolymer particles that are connected by intermolecular covalent bonds, thereby forming a gel organosol.

The gel organosols provide a new approach to improving the sedimentation and redispersion properties of pigmented inks. The method of inducing gelation does not require manipulation of the relative difference in solubility parameter between the graft stabilizer and the carrier solvent into a range (solubility parameter difference

14   greater than 2.5 MPa$^{1/2}$) that acts to reduce agglomeration stability of the graft copolymer. This allows the ink formulator increased flexibility in selection of monomer components of the graft stabilizer, as well as greater flexibility in carrier fluid selection.

For example, side-chain crystallizable monomers that have a high degree of solubility in the carrier solvent may be incorporated into the graft stabilizer without sacrificing gelation characteristics. The use of crystallizable polymeric moieties to

21   improve the durability of non-gel organosol inks has been disclosed in U.S. 5,886,067. Heretofore, the use of such crystallizable polymeric moieties at high weight percentages in a graft stabilizer has prevented the formation of gel organosols owing to the relative solubility parameter difference between the graft stabilizer and the carrier solvent falling in the range of good solubility (0-2.5 MPa$^{1/2}$). It would be advantageous to combine the characteristics of a gel organosol and a controlled-crystallinity organosol into a single graft copolymer composition.

28   The covalently crosslinked gel organosols are particularly useful for their ability to form a three dimensional gel of controlled rigidity which can be reversibly reduced to a fluid state by shearing or heating the organosol or an ink composition containing the organosol. The gels impart useful properties to the liquid ink, notably improved sedimentation stability of the colorant, without compromising print quality

r ink transfer performance. The inks formulated with the gels also exhibit improved redispersion characteristics upon settling, and do not form dilatant sediments such as those formed by non-gelled organosol inks. These characteristics of gel inks facilitate preparation and use of high solids ink concentrates (greater than 2% by weight solids, more preferably greater than 10% by weight solids), thus providing an increased number of printed pages or images from a given volume of ink.

7   The liquid inks will be described below with respect to electrophotographic printing; however, it is to be understood that these liquid inks are not limited in their utility and may also be employed in other electrographic printing processes, high speed printing presses, photocopying apparatus, microfilm reproduction devices, facsimile printing, ink jet printer, instrument recording devices, and the like.

The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and

14   advantages of the invention will be apparent from the description and drawings, and from the claims.

DETAILED DESCRIPTION

A liquid ink composition is provided comprising a colorant and an gel organosol dispersed in a liquid or liquid blend having a Kauri-Butanol (KB) number less than 30. The liquid ink composition is resistant to sedimentation and is capable of rapidly self-fixing, which is particularly useful in electrophotographic, ionographic,

21   or electrostatic imaging and conventional printing processes.

The gel is an amphipathic copolymeric gel comprised of a soluble or marginally insoluble high molecular weight (co)polymeric steric stabilizer which is slightly crosslinked and covalently bonded to an insoluble, thermoplastic (co)polymeric core. The covalently bonded graft steric stabilizer is covalently crosslinked to such an extent that it behaves as an extremely high molecular weight copolymer near its incipient phase separation point in the dispersant liquid. The

28   crosslinked graft stabilizer remains in a freely flowing, easily handled solution until the graft stabilizer is covalently bonded to the insoluble core, at which point a gel organosol is formed.

Gel organosols are dispersions in which the attractive interactions between the elements of the dispersed phase are so strong that the whole system develops a rigid network structure and, under small stresses, behaves elastically. The characteristic of organosol gelation is visibly apparent to one skilled in the art. The crosslinked gel organosols rapidly gel to form a voluminous polymer sediment and a substantially clear supernatant layer of carrier liquid upon standing.

7   Gelation of the graft copolymer organosol is induced by forming covalent bonds between a plurality of graft stabilizer chains which are subsequently or concomitantly grafted to an insoluble core. Crosslinking is effected using a polyfunctional crosslinking agent, i.e. a crosslinkable polymerizable compound containing a plurality of polymerizable moieties. The crosslinkable polymerizable compound may have all of its reactive groups comprising the same chemical moiety, or alternatively, one or more of the reactive groups may be different or distinct from

14   the others. For convenience, we will refer to crosslinkable polymerizable compounds having a single type of chemical moiety comprising its reactive groups as a symmetrical crosslinkable polymerizable compound. We will refer to crosslinkable polymerizable compounds having at least two different and distinct chemical moieties comprising its reactive groups as an asymmetrical crosslinkable polymerizable compound.

The strength of the gel (and hence sedimentation resistance of the ink) can be

21   readily manipulated by controlling the extent to which the graft stabilizer is crosslinked. Greater gel strength (greater sedimentation resistance) is obtained by increasing the crosslink density (percentage of crosslinker) of the graft stabilizer.

Superior stability of the dispersed toner particles with respect to aggregation is obtained when at least one of the polymers or copolymers (denoted as the stabilizer) is an amphipathic substance containing at least one oligomeric or polymeric component of molecular weight at least 500 that is solvated by the carrier liquid. In other words,

28   the selected stabilizer, if present as an independent molecule, would have some finite solubility in the carrier liquid.

The solubility of a material in a given solvent may be predicted from the absolute difference in Hildebrand solubility parameter of the solute relative to the

solvent. The solutes will exist as true solutions or in a highly solvated state when the absolute difference in Hildebrand solubility parameter is less than approximately 1.5 $MPa^{1/2}$. When the absolute difference in Hildebrand solubility parameter exceeds approximately 3.0 $MPa^{1/2}$, the solute will phase separate from the dispersant, forming a solid, insoluble, non-flowing, non-gelled mass. Those solutes having an absolute difference in Hildebrand solubility parameters between 1.5 $MPa^{1/2}$ and 3.0 $MPa^{1/2}$ are

7   considered to be weakly solvated or marginally insoluble.

The solubility parameters of the graft stabilizers, as well as the carrier liquids in which the stabilizers are dispersed, are calculated using values for the Hildebrand solubility parameter of the monomers used to prepare the graft stabilizer and the carrier liquids obtained using the group contribution method developed by Small, P. A., J. Appl. Chem., 3, 71 (1953) using Small's group contribution values listed in Table 2.2 on page VII/525 in the Polymer Handbook, 3rd Ed., J. Brandrup & E. H.

14   Immergut, Eds. John Wiley, NY, pp 519-557 (1989). The Hildebrand solubility parameter for a copolymer may be calculated using a volume fraction weighting of the individual Hildebrand solubility parameters for each monomer comprising the copolymer. Similarly, the Hildebrand solubility parameter for a mixture may be calculated using a volume fraction weighting of the individual Hildebrand solubility parameters for each component of the mixture. Thus, the Hildebrand solubility parameter for a mixture of solvents or polymerizable compounds may be calculated

21   using a volume fraction weighting of the individual Hildebrand solubility parameters for each chemical compound comprising the solvent mixture.

Table 1 lists the Hildebrand solubility parameters for some common carrier liquids used in an electrophotographic toner and the Hildebrand solubility parameters and glass transition temperatures for some common monomers used in synthesizing organosols.

Table I   Hildebrand Solubility Parameters

Solvent Values at 25°C

Solvent Commercial Trade Designation	Kauri-Butanol Number by ASTM Method D1133-54T (mL)	Hildebrand Solubility Parameter (MPa$^{1/2}$)
NORPAR 15	18	13.99
NORPAR 13	22	14.24
NORPAR 12	23	14.30
ISOPAR V	25	14.42
EXXSOL D80	28	14.60

Source: Calculated from equation #31 of Polymer Handbook, 3rd Ed., J.

Brandrup E.H. Immergut, Eds. John Wiley, NY, p. VII/522 (1989).

M n mer Values at 25°C

Monomer Name	Hildebrand Solubility Parameter (MPa$^{1/2}$)	Glass Transition Temperature (°C)*
n-Octadecyl Methacrylate	16.77	-100
n-Octadecyl Acrylate	16.82	-55
Lauryl Methacrylate	16.84	-65
Lauryl Acrylate	16.95	-30
2-Ethylhexyl Methacrylate	16.97	-10
2-Ethylhexyl Acrylate	17.03	-55
n-Hexyl Methacrylate	17.13	-5
t-Butyl Methacrylate	17.16	107
n-Butyl Methacrylate	17.22	20
n-Hexyl Acrylate	17.30	-60
n-Butyl Acrylate	17.45	-55
Ethyl Methacrylate	17.90	66
Ethyl Acrylate	18.04	-24
Methyl Methacrylate	18.17	105
Vinyl Acetate	19.40	30
Methyl Acrylate	20.2	5

Calculated using Small's Group Contribution Method, Small, P.A. Journal of Applied Chemistry 3 p. 71 (1953). Using Group Contributions from Polymer Handbook, 3rd Ed., J. Brandrup E.H. Immergut, Eds., John Wiley, NY, p. VII/ 525 (1989).

7   * Polymer Handbook, 3rd Ed., J. Brandrup E.H. Immergut, Eds., John Wiley, NY, pp. VII/209-277 (1989).

The carrier liquid may be selected from a wide variety of materials that are known in the art, but preferably has a Kauri-Butanol number less than 30. The liquid is typically oleophilic, chemically stable under a variety of conditions, and electrically insulating. Electrically insulating refers to a liquid having a low dielectric constant

and a high electrical resistivity. Preferably, the liquid has a dielectric constant of less than 5, more preferably less than 3. Electrical resistivities of carrier liquids are typically greater than 10^9 Ohm-cm, more preferably greater than 10^{10} Ohm-cm. The carrier liquid preferably is also relatively nonviscous to allow movement of the charged particles during development, and sufficiently volatile to permit its removal from the final imaged substrate, but sufficiently non-volatile to minimize evaporative losses in the developer. In addition, the carrier liquid should be chemically inert with respect to the materials or equipment used in the liquid electrophotographic process, particularly the photoreceptor and its release surface.

Examples of suitable carrier liquids include aliphatic hydrocarbons (n-pentane, hexane, heptane and the like), cycloaliphatic hydrocarbons (cyclopentane, cyclohexane and the like), aromatic hydrocarbons (benzene, toluene, xylene and the like), halogenated hydrocarbon solvents (chlorinated alkanes, fluorinated alkanes, chlorofluorocarbons, and the like), silicone oils and blends of these solvents. Preferred carrier liquids include branched paraffinic solvent blends such as those commercially available under the trade designations ISOPAR G, ISOPAR H, ISOPAR K, ISOPAR L, ISOPAR M and ISOPAR V (all available from Exxon Corporation, NJ), and most preferred carriers are the aliphatic hydrocarbon solvent blends such as those commercially available under the trade designations NORPAR 12, NORPAR 13 and NORPAR 15 (all available from Exxon Corporation, NJ).

The organosol is a graft copolymer prepared by chemically bonding a generally soluble (co)polymer to a generally insoluble (co)polymer resin core. Any number of reactions known to those skilled in the art may be used to effect grafting of the soluble polymeric stabilizer to the organosol core during free radical polymerization. Common grafting methods include random grafting of polyfunctional free radicals; ring-opening polymerizations of cyclic ethers, esters, amides or acetals; epoxidations; reactions of hydroxyl or amino chain transfer agents with terminally-unsaturated end groups; esterification reactions (i.e., glycidyl methacrylate undergoes tertiary-amine catalyzed esterification with methacrylic acid); and condensation polymerization.

The composition of the graft stabilizer is normally selected such that the Hildebrand Solubility Parameter of the graft stabilizer (shell) closely matches that of

14

the carrier liquid in order to ensure that the stabilizer will be sufficiently solvated to dissolve in the carrier solvent. Virtually any polymerizable compound that exhibits a Hildebrand Solubility Parameter difference less than 3.0 MPa$^{1/2}$ relative to the carrier liquid may be used in forming a graft stabilizer. In addition, polymerizable compounds that exhibit a Hildebrand Solubility Parameter difference greater than 3.0 MPa$^{1/2}$ relative to the carrier liquid may be used in forming a copolymeric graft

7   stabilizer, provided that the effective Hildebrand Solubility Parameter difference for the stabilizer is less than 3.0 MPa$^{1/2}$ relative to the carrier liquid. The absolute difference in Hildebrand Solubility Parameter between the graft stabilizer (shell) and the carrier liquid is preferably less than 2.6 MPa$^{1/2}$.

Preferred polymerizable compounds useful in forming the graft stabilizer are the C_6-C_{30} acrylic and methacrylic esters. Examples of suitable polymerizable compounds for use in the graft stabilizer composition non-exclusively include

14   monomers such as, hexyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl (lauryl) acrylate, octadecyl (stearyl) acrylate, behenyl acrylate, hexyl methacrylate, 2-ethylhexyl(methacrylate), decyl acrylate, dodecyl (lauryl) methacrylate, octadecyl (stearyl) methacrylate and other alkyl acrylates and methacrylates.

Preferrably, the polymerizable compounds are also crystallizable compounds having crystallization (melting) temperatures above room temperature (25°C). Such crystallizable, polymerizable compounds are particularly useful in forming graft

21   stabilizers that yield organosols and inks exhibiting improved image durability, including blocking and erasure resistance. Crystallizable, polymerizable compounds suitable for incorporation into a graft stabilizer include >C_{14} acrylic and methacrylic esters. Preferable crystallizable, polymerizable compounds include octadecyl acrylate and behenyl acrylate.

Other monomers, macromers, or polymers may be used either alone or in conjunction with the aforementioned materials, including melamine and melamine

28   formaldehyde resins, phenol formaldehyde resins, epoxy resins, polyester resins, styrene and styrene/acrylic copolymers, acrylic and methacrylic esters, cellulose acetate and cellulose acetate-butyrate copolymers, and poly(vinyl butyral) copolymers.

Preferred molecular weight ranges for the graft stabilizer are 5,000-1,000,000
Daltons (Da), more preferably = 50,000-500,000 Da, most preferably = 150,000-
250,000 Da. The polydispersity of the graft stabilizer also has an affect on imaging
and transfer performance of the liquid toners. Generally, it is desirable to maintain the
polydispersity (the ratio of the weight-average molecular weight to the number
average molecular weight) of the graft stabilizer below 15, more preferably below 5,
7   most preferably below 2.5.

The crosslinkable polymerizable compound which is added to the graft
stabilizer has a functionality of 2. The crosslinkable polymerizable compound may
have all of its reactive groups comprising the same chemical moiety ("symmetrical
crosslinkable polymer compound"), or alternatively, one or more of the reactive
groups may be different or distinct from the others ("asymmetrical crosslinkable
polymer compound").

14   Preferably, the crosslinkable polymerizable compound is symmetrical; this
allows the crosslinking reaction to occur in a single step, generally corresponding to
the polymerization step forming the graft stabilizer. Preferably, this crosslinking
reaction occurs via free radical polymerization, although other crosslinking reactions
may be used. Nonlimiting examples of suitable non-radical crosslinking reactions
include the reaction of an isocyanate to a hydroxy-group to form a polyurethane
linkage, the reaction of an isocyanate to an amino-group to form a polyurea linkage,
21   and the reaction of glycidyl methacrylate with an acrylic acid-group to form an
epoxide linkage.

It is also possible to use an asymmetrical crosslinkable polymerizable
compound in a process in which one reactive functional moiety of the asymmetrical
crosslinkable compound is covalently bonded to the soluble backbone during
polymerization to form the graft stabilizer. Concomitantly or subsequently, the
second reactive functional moiety of the asymmetrical crosslinkable compound is
28   covalently bonded between graft stabilizer molecules using a reaction mechanism
distinct from that used to covalently bond the crosslinkable compound into the graft
stabilizer. The net effect is to form intermolecular crosslinks (covalent bonds)
between graft stabilizer molecules.

16

Suitable bi-functional symmetric monomers include divinyl benzene; 1,3 butanediol diacrylate; 1,4 butanediol diacrylate; 1,3 butanediol dimethacrylate; diethylene glycol diacrylate; diethylene glycol dimethacrylate; ethoxylated Bisphenol A diacrylate; ethoxylated Bisphenol A dimethacrylate; ethylene glycol dimethacrylate (EGDMA); 1,6 hexanediol diacrylate; 1,6 hexanediol dimethacrylate; neopentyl glycol diacrylate; neopentyl glycol dimethacrylate; polyethylene glycol diacrylate;

7   polyethylene glycol dimethacrylate; propoxylated neopentyl glycol diacrylate; tetraethylene glycol diacrylate; tetraethylene glycol dimethacrylate; triethylene glycol diacrylate; triethylene glycol dimethacrylate; tripropylene glycol diacrylate; tripropylene glycol dimethacrylate; zinc diacrlyate; zinc dimethacrylate and 1,4 phenylene diisocyanate (PDI).

Suitable bi-functional asymmetric monomers include to t-butylaminoethyl methacrylate; diethylaminoethyl acrylate; ; diethylaminoethyl methacrylate; 2-

14   diisopropylaminoethyl methacrylate; 2-dimethylaminoethyl methacrylate; dimethylaminopropyl methacrylamide; dipentaerthritol monohydroxypentaacrylate; 2,3-epoxypropyl methacrylate (glycidyl methacrylate); 4-hydroxybutyl acrylate; 2-hydroxyethyl acrylate; 2-hydroxyethyl methacrylate; 2-hydroxypropyl acrylate; cinnamyl alcohol; allyl mercaptan, methallylamine; azlactones, such as 2-alkenyl-4,4-dialkylazlactone; 2-hydroxypropyl methacrylate; meta-isopropenyldimethylbenzyl isocyanate (TMI); isocyanatoethylmethacrylate (IEM); trimethylsilylmethacrylate;

21   (trimethylsilylmethyl)methacrylate; n-vinyl caprolactam; 2-vinyl pyridine; 4-vinyl pyridine and N-vinyl-2-pyrrolidone.

Suitable tri-functional symmetric monomers include ethoxylated trimethylolpropane triacrylate; glyceryl propoxy triacrylate; pentaerythritol triacrylate; trimethylolpropane triacrylate; trimethylolpropane trimethacrylate (TTMA); and tris(2-hydroxyethyl)isocyanurate triacrylate). A suitable tetra-functional crosslinkable polymerizable compound is pentaerythritol tetraacrylate.

28   Crosslinking of the graft stabilizer may result from any number of well known polymerization crosslinking reactions, including reaction of polyfunctional free radicals; group transfer polymerizations, ring-opening polymerizations of cyclic ethers, esters, amides or acetals; epoxidations; reactions of hydroxyl or amino chain transfer agents with terminally-unsaturated end groups; esterification reactions (i.e.,

17

glycidyl methacrylate undergoes tertiary-amine catalyzed esterification with methacrylic acid); and condensati n p lymerization (e.g., isocyanates react with amines to form polyureas; isocyanates react with hydroxyl groups to form polyurethanes).

The extent of gelation of the crosslinked gel organosol may be controlled by manipulating the concentration of crosslinkable, polymerizable compound

7   incorporated into the graft stabilizer. Generally, a higher concentration of crosslinkable, polymerizable compound leads to a higher crosslink density and therefore a stronger gel. However, too high a concentration of crosslinkable, polymerizable monomer will cause the graft stabilizer to solidify into a very high molecular weight, insoluble polymer that is not suitable for incorporation into a crosslinked gel organosol. Preferably 0.1-2.0% w/w, more preferably 0.25-1.5% w/w, most preferably 0.5-1.0% w/w is used when divinylbenzene is the crosslinkable,

14   polymerizable compound. However, the preferred concentration range of crosslinkable polymerizable compound will vary somewhat depending on the specific crosslinkable, polymerizable compound.

As discussed above, the organosol is a graft copolymer dispersion formed by covalently bonding the graft stabilizer to an insoluble resin core, either subsequent to or concomitant with crosslinking the graft stabilizer. The grafting reaction generally occurs between a grafting site incorporated into the graft stabilizer and a reaction site

21   in the polymerizing or polymerized core. Preferably, the grafting reaction proceeds by reaction of an isocyanate to a hydroxyl group to form a urethane linkage between the stabilizer and the core. The grafting site is preferably formed by incorporating hydroxyl groups into the graft stabilizer during a first free radical polymerization and catalytically reacting all or a portion of these hydroxyl groups with an ethylenically unsaturated aliphatic isocyanate (e.g. meta-isopropenyldimethylbenzyl isocyanate [TMI] or isocyanatoethylmethacrylate [IEM]) to form a polyurethane linkage during a

28   subsequent non-free radical reaction step. The graft stabilizer is then covalently bonded to the nascent insoluble acrylic (co)polymer core via reaction of the unsaturated vinyl group of the grafting site with ethylenically-unsaturated core monomers (e.g. vinyl esters, particularly acrylic and methacrylic esters with carbon numbers < 6 or vinyl acetate; vinyl aromatics, such as styrene; acryl nitrile; n-vinyl

pyrrolid ne; vinyl chloride and vinylidene chloride) during a subsequent free radical polymerization step.

Other methods of effecting grafting of the preformed polymeric stabilizer to the incipient insoluble core particle are known to those skilled in the art. For example, alternative grafting protocols are described in sections 3.7-3.8 of Barrett <u>Dispersion Polymerization in Organic Media</u>, K. E. J. Barrett, ed., (John Wiley: New York, 1975), pp. 79-106. A particularly useful method for grafting the polymeric stabilizer to core utilizes an anchoring group. The function of the anchoring groups is to provide a covalent link between the core part of the particle and the soluble component of the steric stabilizer. Suitable monomers containing anchoring groups include: adducts of alkenylazlactone comonomers with an unsaturated nucleophile containing hydroxy, amino, or mercaptan groups, such as 2-hydroxyethylmethacrylate, 3-hydroxypropylmethacrylate, 2-hydroxyethylacrylate, pentaerythritol triacrylate, 4-hydroxybutyvinylether, 9-octadecen-1-ol, cinnamyl alcohol, allyl mercaptan, methallylamine; and azlactones, such as 2-alkenyl-4,4-dialkylazlactone of the structure
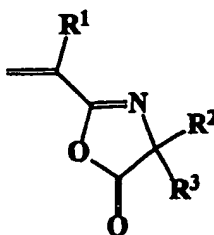
where R^1 = H, or alkyl having 1 to 5 carbons, preferably one carbon, R^2 and R^3 are independently lower alkyl groups having 1 to 8 carbons, preferably 1 to 4 carbons.

Most preferably, however, the grafting mechanism is accomplished by grafting an ethylenically-unsaturated isocyanate (e.g., dimethyl-m-isopropenyl benzylisocyanate, available from American Cyanamid) to hydroxyl groups previously incorporated into the graft stabilizer precursor (i.e., hydroxy ethyl methacrylate).

The insoluble organosol core is the dispersed phase of the graft copolymer dispersion. The core polymer is generally made *in situ* by copolymerization with the stabilizer monomer. The solubility parameter of the core is generally chosen such that

it differs substantially from that f the dispersi n medium in order to ensure that the core m nomers will phase separate during dispersion polymerization (forming the core). Virtually any monomer or combination of monomers may be used in forming the organosol core, provided that the core as a whole is insoluble in the carrier liquid. Preferably, the Hildebrand solubility parameter difference between the core as a whole and the carrier liquid exceeds 3.0 MPa$^{1/2}$. Examples of polymerizable

7   compounds suitable for use in the organosol core include C_1-C_5 acrylate and methacrylate esters such as, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate), butyl methacrylate, styrene and vinyl acetate.

Monomers which individually are very soluble in the dispersant medium may also be incorporated into the core in small amounts with monomers which, when polymerized, are not very soluble in the carrier liquid. The effect of incorporating a monomer having good solubility in the carrier liquid into the organosol core will

14   generally be to cause carrier liquid absorption or swelling of the core. This can be particularly useful when higher core T_g's are desired, for example, to improve image durability, but when rapid self-fixing of the ink is still required in the imaging process. By increasing the affinity of the core for the carrier liquid, the carrier liquid will be imbibed into the core and may act to plasticize the core, permitting rapid self-fixing of an ink comprising a high core T_g organosol even at temperatures below the normal minimum film-forming temperature.

21   Preferably, the Hildebrand solubility parameter difference between the core as a whole and the carrier liquid exceeds 3.0 MPa$^{1/2}$. The amount of soluble monomer incorporated into the core typically ranges between 1-30% w/w, more preferably 5-20% w/w. Examples of soluble polymerizable compounds suitable for use in the organosol core include C_6-C_{30} acrylate and methacrylate esters such as cyclohexyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl (lauryl) acrylate, octadecyl (stearyl) acrylate, behenyl acrylate, cyclohexyl methacrylate, hexyl

28   methacrylate, 2-ethylhexyl(methacrylate), decyl acrylate, dodecyl (lauryl) methacrylate, octadecyl (stearyl) methacrylate and other acrylates and methacrylates which meet the solubility parameter requirements described above.

In selecting polymerizable compounds for use in the organosol core, it is necessary to consider not only their effect on solubility parameter difference between

20

the core and the carrier liquid, but also their effect n the effective glass transition temperature of the core and the resulting impact on imaging performance. Preferably, the Tg of the core is < 30°C to allow an ink composition containing the resin as a major component to undergo rapid film formation (rapid self-fixing) in printing or imaging processes carried out at temperatures greater than the core T_g, preferably at or above 23°C. Rapid self-fixing assists in avoiding printing defects (such as

7   smearing or trailing-edge tailing) and incomplete transfer in high speed printing. The use of low T_g thermoplastic polymeric binders to promote film formation is described in Z.W. Wicks, *Film Formation*, Federation of Societies for Coatings Technologies, p 8 (1986).

The T_g can be calculated for a (co)polymer using known values for the high molecular weight homopolymers (Table I) and the Fox equation expressed below:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3} + ...$$

14   where w_i is the weight fraction of monomer "i" and T_{gi} is the glass transition temperature of the high molecular weight homopolymer of monomer "i" as described in Wicks, A.W., F.N. Jones & S.P. Pappas, Organic Coatings, 1, John Wiley, NY, pp 54-55 (1992).

Another reason for using polymer particles in which the core has a T_g<30°C is that these particles can coalesce into a resinous film at room temperature. The overprinting capability of a toner is related to the ability of the polymer particles to

21   deform and coalesce into a resinous film during the air drying cycle of the electrophoretically deposited toner particles. The coalescent particles permit the electrostatic latent image to discharge during the imaging cycle so another image can be overprinted. On the other hand, non-coalescent particles retain their shape even after being air dried on the photoreceptor. The points of contact are then few compared to a homogeneous or continuous film-forming latex, and as a result, some of the charges are retained on the unfused particles, repelling the next toner.

28   A toner layer made of polymer particles having a core with a T_g>30°C may be made to coalesce into a film at room temperature if the stabilizer/core ratio is high enough. Thus the choice of stabilizer/(core + stabilizer) ratios in the range 20 wt.% to 80 wt.% can give coalescence at room temperature with core T_g values in a corresponding

range 25°C to 105°C. With a core T_g<30°C, the preferred range of stabilizer/(core + stabilizer) ratio is 10 to 40 wt.%.

The integrity of the toned image during partial removal of the solvent also depends upon the core T_g, with lower T_g promoting film strength and image integrity at the cost of additional image tack. An organosol core T_g below room temperature is preferred to ensure that the toner will in fact film form. Preferably, the minimum film

7   forming temperatures are between about 5-45°C and the organosol core T_g is below room temperature to allow the toner to form a film and maintain good image integrity during solvent removal and good cohesive strength during image transfer from the photoconductor onto either a transfer medium or receptor.

To yield the best offset transfer efficiency without causing excessive residual tack and blocking of the transferred image, an organosol core having a T_g between - 10 and 20°C is preferred, more preferably between -5 and 15°C. Under constant

14   transfer roll pressure conditions, lower core T_g organosols exhibit 100% transfer at lower temperatures than high T_g organosols. Toner transfer is dependent upon the extent of self-fixing or dryness of the toner film. In addition, toned images will require some finite drying time in order to allow film formation to occur. This drying can be accelerated by using heated air, vacuum drying, an electrostatically-biased or unbiased squeegee (to hydraulically remove excess dispersant), or other similar methods known in the art, e.g., the system described in U.S. Patent No. 5,300,990.

21   The rate of film formation (self-fixing) may also be accelerated by adding a plasticizer to the toned image to effectively lower the minimum film forming temperature.

Residual image tack after transfer may be adversely affected by the presence of high tack monomers, such as ethyl acrylate, in the organosol. In addition, the cohesive strength and durability of the ink film generally decreases as the organosol core T_g decreases. Ideally, organosol core T_g would be selected to be as high as

28   possible in order to reduce residual tack and maximize image durability. However, this is often not practical, particularly for liquid inks used in imaging processes in which the inks are required to form a film at room temperature. Consequently, organosols are generally formulated such that the organosol core preferably has a

22

glass transition temperature (T_g) less than high room temperature (30°C) but greater than -10°C.

The organosol core comprises approximately 30-95% of the organosol on a weight basis. Thus, the core's T_g will typically dominate over the stabilizer's T_g and the organosol T_g may be taken as a first approximation to be the core T_g. As illustrated supra, a simple algebraic method based upon a composition-weighted sum

7   of inverse T_g's (using absolute temperatures) can be used to calculate the effective T_g of a copolymer blend used to make up an organosol core. Similar arguments allow an assumption that the solubility parameter of the stabilizer will generally control the stability of the organosol. Therefore, the stabilizer solubility parameter is preferably selected to closely match that of the dispersant for maximum aggregation stability.

Using the data in Table 1 and applying the above criteria, it is noted that polymerizable compounds such as methyl acrylate, ethyl acrylate, and vinyl acetate

14   are most suitable for incorporation into an organosol core comprising a single polymerizable compound exclusive of the grafting compound (T_g between -30 and 30°C, and solubility parameter difference relative to the solvents NORPAR 12 greater than 3.0 MPa$^{1/2}$). Preferably, the core comprises a copolymer of at least one high glass transition temperature polymerizable compound, such as methyl methacrylate, ethyl methacrylate or butyl methacrylate; and at least one low glass transition polymerizable compound such as ethyl acrylate or butyl acrylate. This allows

21   variation of the core T_g over a wide range between T_g's of the respective polymerizable compounds by simple variation of the relative weight ratios of the high and low T_g polymerizable compounds, as calculated using the Fox Equation.

The preferred polymerizable compounds for use in making a copolymer core in NORPAR 12 carrier liquid are methyl methacrylate and ethyl acrylate, since these monomers individually or in any weight ratio exceed the 3.0 MPa$^{1/2}$ Hildebrand solubility parameter difference relative to NORPAR 12 and will therefore readily

28   form an insoluble core in this carrier liquid upon polymerization. In addition, ethyl acrylate and methyl methacrylate permit the variation of the core T_g anywhere within the range -24°C to 105°C merely by varying the relative weight ratios of the two monomers in the core.

A preferred rgan sol core composition contains about 75 weight percent ethyl acrylate and 25 weight percent methyl methacrylate, yielding a calculated core T_g of -1°C. This permits the toners to rapidly self-fix under normal room temperature or higher development conditions and also produce tack-free fused images that resist blocking at room temperature.

Other polymers which may be used either alone or in conjunction with the aforementioned materials, include melamine and melamine formaldehyde resins, phenol formaldehyde resins, epoxy resins, polyester resins, styrene and styrene/acrylic copolymers, acrylic and methacrylic esters, cellulose acetate and cellulose acetate-butyrate copolymers, and poly(vinyl butyral) copolymers.

If the core/shell ratio is too high, there may be insufficient graft stabilizer present to sterically-stabilize the organosol with respect to aggregation. If the core/shell ratio is too low, the polymerization may have insufficient driving force to form a distinct particulate phase resulting in a copolymer solution, not a self-stable organosol dispersion. The optimal weight ratio of the resin core to the stabilizer shell is on the order of 1/1 to 15/1, preferably between 2/1 and 10/1, and most preferably between 4/1 and 8/1.

The particle size of the organosol also influences the imaging, drying, and transfer characteristics of the liquid inks. Preferably, the primary particle size (determined with dynamic light scattering) of the organosol is between about 0.05 and 5.0 microns, more preferably between 0.15 and 1 micron, most preferably between 0.20 and 0.50 microns.

A liquid ink utilizing the aforementioned gel organosol comprises colorant particles embedded in the thermoplastic organosol resin. Useful colorants are well known in the art and include materials such as dyes, stains, and pigments. Preferred colorants are pigments that may be incorporated into the polymer resin, are nominally insoluble in and nonreactive with the carrier liquid, and are useful and effective in making visible the latent electrostatic image. Examples of suitable colorants include: phthalocyanine blue (C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4 and 16), monoarylide yellow (C.I. Pigment Yellow 1, 3, 65, 73 and 74), diarylide yellow (C.I. Pigment Yellow 12, 13, 14, 17 and 83), arylamide (Hansa) yellow (C.I. Pigment Yellow 10,

97, 105 and 111), Pigment Yellow 138, azo red (C.I. Pigment Red 3, 17, 22, 23, 38, 48:1, 48:2, 52:1, 81, 81:1, 81:2, 81:3 and 179), quinacridone magenta (C.I. Pigment Red 122, 202 and 209) and black pigments such as finely divided carbon (Cabot Monarch 120, Cabot Regal 300R, Cabot Regal 350R, Vulcan X72) and the like.

For some applications, it is desirable to use the organosol without an added colorant (dye or pigment) to provide a clear protective overcoat for an underlying image on a permanent receptor. In such cases, the transparent ink may be applied, for example, using well-known coating or electrographic development processes, onto either a temporary imaging receptor or permanent imaging receptor. In the event that the transparent organosol is applied to a permanent image receptor, the organosol should be coated onto the surface of the receptor and any underlying image in order to perform as a protective overcoat. In the event that the organosol is applied to a temporary image receptor, consideration must be given to the reversal of layers which occurs during offset transfer processes. Thus, it may be necessary to coat or develop the transparent organosol as the first layer on a photoreceptive element upon which a multi-colored image is constructed in order to insure that the transparent organosol acts as a protective topcoat upon offset transfer of the image to a permanent image receptor.

The optimal weight ratio of resin (organosol) to colorant in the toner particles is on the order of 1/1 to 20/1, preferably between 3/1 and 10/1, and most preferably between 5/1 and 8/1. The total dispersed material in the carrier liquid typically represents 0.5 to 70 weight percent, preferably between 1 and 25 weight percent, most preferably between 2 and 17 weight percent of the total liquid developer composition.

The gel organosols can be used to fabricate liquid electrophotographic toners that exhibit excellent imaging characteristics in liquid immersion development. For example, the gel organosol liquid toners exhibit low bulk conductivity, low free phase conductivity, and low charge/mass and high mobility, all of which are desirable characteristics for producing high resolution, background-free images with high optical density. In particular, the low bulk conductivity, low free phase conductivity, and low charge/mass of the toners allow them to achieve high developed optical density over a wide range of solids concentrations, thus improving their extended printing performance relative to conventional toners. In addition, color liquid toners

25

based upon these gel organosols on development form transparent films that transmit incident light, consequently allowing the photoconductor layer to discharge.

The toners have low T_g values with respect to most available toner materials. This enables the toners to form films at room temperature. It is not necessary for any specific drying procedures or heating elements to be present in the apparatus. Normal room temperature (19-20°C) is sufficient to enable film forming, and as is the ambient

7   internal temperature of the apparatus during operation which tends to be at a higher temperature (e.g., 25-40°C) even without specific heating elements. It is possible to have the apparatus operate at an internal temperature of 40°C or less at the toning station and immediately thereafter where a fusing operation would ordinarily be located.

The gel organosol liquid toners also exhibit improved transfer characteristics relative to conventional inks used in the art, particularly with offset transfer processes. The rapid-fixing characteristics of the toners permit their use in liquid

14 development/dry adhesive offset transfer imaging processes, such as the processes described in U.S. 5,650,253 and 5,916,718. Dry adhesive transfer eliminates the need for coronas or other charging devices to electrostatically assist transfer of a wet image from the imaging surface to the preferred substrate. In addition, dry adhesive transfer of the toner further reduces carry-out of excessive solvent vapors with the image, as would occur with conventional electrostatically-assisted transfer processes.

An electrophotographic liquid toner may be formulated by incorporating a

21 charge control agent into the liquid ink. The charge control agent, also known as a charge director, provides uniform charge polarity of the toner particles. The charge director may be incorporated into the toner particles using a variety of methods such as chemically reacting the charge director with the toner particle, chemically or physically adsorbing the charge director onto the toner particle (resin or pigment), or chelating the charge director to a functional group incorporated into the toner particle. A preferred method is via a functional group built into the graft stabilizer. The charge

28 director imparts an electrical charge of selected polarity onto the toner particles. Any number of charge directors described in the art may be used. For example, the charge director may be introduced in the form of metal salts consisting of polyvalent metal ions and organic anions as the counterion. Suitable metal ions include Ba(II), Ca(II), Mn(II), Zn(II), Zr(IV), Cu(II), Al(III), Cr(III), Fe(II), Fe(III), Sb(III), Bi(III), Co(II),

La(III), Pb(II), Mg(II), Mo(III), Ni(II), Ag(I), Sr(II), Sn(IV), V(V), Y(III), and Ti(IV). Suitable organic ani ns include carboxylates or sulf nates derived from aliphatic or aromatic carboxylic or sulfonic acids, preferably aliphatic fatty acids such as stearic acid, behenic acid, neodecanoic acid, diisopropylsalicylic acid, octanoic acid, abietic acid, naphthenic acid, octanoic acid, lauric acid, tallic acid, and the like. Preferred positive charge directors are the metallic carboxylates (soaps) described in U.S. Patent

7   3,411,936, which include alkaline earth- and heavy-metallic salts of fatty acids containing at least 6-7 carbons and cyclic aliphatic acids including naphthenic acid; more preferred are polyvalent metal soaps of zirconium and aluminum; most preferred is the zirconium soap of octanoic acid (Zirconium HEX-CEM from Mooney Chemicals, Cleveland, OH).

The preferred charge direction levels for a given toner formulation will depend upon a number of factors, including the composition of the graft stabilizer and

14   organosol, the molecular weight of the organosol, the particle size of the organosol, the core/shell ratio of the organosol, the pigment used in making the toner, and the ratio of organosol to pigment. In addition, preferred charge direction levels will also depend upon the nature of the electrophotographic imaging process, particularly the design of the developing hardware and photoreceptive element. Those skilled in the art, however, know how to adjust the level of charge direction based on the listed parameters to achieve the desired results for their particular application.

21   The conductivity of a liquid toner has been well established in the art as a measure of the effectiveness of a toner in developing electrophotographic images. A range of values from 1.0×10^{-11} mho/cm to 10.0×10^{-11} mho/cm has been disclosed as advantageous in U.S. 3,890,240. High conductivities generally indicate inefficient association of the charges on the toner particles and are seen in the low relationship between current density and toner deposited during development. Low conductivities indicate little or no charging of the toner particles and lead to very low development

28   rates. The use of charge director compounds to ensure sufficient charge associated with each particle is a common practice. There has, in recent times, been a realization that even with the use of charge directors there can be much unwanted charge situated on charged species in solution in the carrier liquid. Such charge produces inefficiency, instability and inconsistency in the development. U.S. Patent No. 4,925,766 discloses

that at least 40%, and preferably at least 80%, of the total charge in the liquid toner
should be situated and remain n the toner particles.

Suitable efforts to localize the charges onto the toner particles and to ensure that
there is substantially no migration of charge from those particles into the liquid, and that
no other unwanted charge moieties are present in the liquid, give substantial
improvements. A measure of the required properties is the ratio between the

7   conductivity of the carrier liquid as it appears in the liquid toner and the conductivity of
the liquid toner as a whole. This ratio is preferably less than 0.6, more preferably less
than 0.4, and most preferably less than 0.3.

Any number of methods may be used for effecting particle size reduction of
the pigment in preparation of the gel liquid toners. Some suitable methods include
high shear homogenization, ball-milling, attritor milling, high energy bead (sand)
milling, basket milling or other means known in the art. Preferably, the ink is milled

14   in an attritor, vertical bead mill, or basket mill to avoid overshearing the organosol,
which can cause an undesirable reduction in ink stability and adversely affect charge
characteristics such as ink conductivity.

In electrophotographic and electrographic processes, an electrostatic image is
formed on the surface of a photoreceptive element or dielectric element. The
photoreceptive element or dielectric element may be an intermediate transfer drum or
belt, or the substrate for the final toned image itself, as described by Schmidt, S. P.

21   and Larson, J. R. in Handbook of Imaging Materials Diamond, A. S., Ed: Marcel
Dekker: New York; Chapter 6, pp 227-252, and U. S. Patent Nos. 4,728,983,
4,321,404, and 4,268,598.

In electrography, a latent image is typically formed by (1) placing a charge
image onto the dielectric element (typically the receiving substrate) in selected areas
of the element with an electrostatic writing stylus or its equivalent to form a charge
image, (2) applying toner to the charge image, and (3) fixing the toned image. An

28   example of this type of process is described in U.S. Patent No. 5,262,259.

Images formed by the present invention may be of a single color or a plurality
of colors. Multicolor images can be prepared by repetition of the charging and toner
application steps. Examples of electrophotographic methods suitable for producing

28

full color reproductions are described by U.S. Patent N s. 2,297,691; 2,752,833; 2,986,466; 3,690,756; 4,403,848; 4,370,047; 4,467,334; 4,728,983; U.S. 5,650,253; U.S. 5,916,718; and European Patent Application No. 0,453,256. Examples of suitable transfer and fixing processes are described in U.S. Patent Nos. 4,337,303 and 5,108,865.

In electrophotography, the electrostatic image is typically formed on a drum or
7   belt coated with a photoreceptive element by (1) uniformly charging the photoreceptive element with an applied voltage, (2) exposing and discharging portions of the photoreceptive element with a radiation source to form a latent image, (3) applying a toner to the latent image to form a toned image, and (4) transferring the toned image through one or more steps to a final receptor sheet. In some applications, it is sometimes desirable to fix the toned image using a heated pressure roller or other fixing methods known in the art.

14   While the electrostatic charge of either the toner particles or photoreceptive element may be either positive or negative, electrophotography is preferably carried out by dissipating charge on a positively charged photoreceptive element. Toner is then applied to the regions in which the positive charge was dissipated using a liquid toner immersion development technique. This development may be accomplished by using a uniform electric field produced by a development electrode spaced near the photoreceptive element surface. A bias voltage is applied to the electrode
21   intermediate to the initially charged surface voltage and the exposed surface voltage level. The voltage is adjusted to obtain the required maximum density level and tone reproduction scale for halftone dots without any background deposited. Liquid toner is then caused to flow between the electrode and the photoreceptive element. The charged toner particles are mobile in the field and are attracted to the discharged areas on the photoreceptive element while being repelled from the undischarged non-image areas. Excess liquid toner remaining on the photoreceptive element is removed by
28   techniques well known in the art. Thereafter, the photoreceptive element surface may be force dried or allowed to dry at the ambient conditions.

Particularly useful electrophotographic processes for forming a multi-colored image on a receptor are described in U.S. 5,061,583, U.S. 5,650,253 and U.S. 5,916,718. The process disclosed in U.S. 5,650,253 basically involves the steps of (i)

applying a uniform positive charge of approximately 700 volts on the surface of a
photoreceptive element, (ii) exposing and partially discharging the surface of the
photoreceptive element with a laser scanning device in an image-wise pattern to
create a latent image, (iii) applying a liquid color toner to the latent image to form
both a toned image and a uniform surface charge on the photoreceptive element, (iv)
removing excess liquid toner, (v) drying the toned image, and (vi) transferring the
7   toned image either directly or indirectly onto a final receptor. To form multi-colored
images, steps (i) through (iv) are repeated until all the desired colors are formed on
the photoreceptive element prior to transferring the images either directly or indirectly
onto a final receptor.

The process disclosed in U.S. 5,916,718 is similar to that of U.S. U.S.
5,650,253, except that processes (ii) through (v) are repeated in forming a multi-
colored image. Unlike conventional electrophotographic processes, this process of
14   forming multi-colored images may be accomplished without erasing the residual
charge and recharging the surface of the photoreceptive element prior to scanning and
developing a subsequent image. The liquid toner of the present invention provides
sufficient charge in the imaged areas to allow the creation of a subsequent latent
image without erasing and recharging the surface. Alternatively, the process of U.S.
5,916,718 may be carried out in a manner such that steps (ii)-(vi) are repeated in
forming a multi-colored image, in which case the multi-colored image may be built up
21   on an intermediate transfer element, or may be built up on the final image receptor.

These methods make use of an offset transfer process incorporating as an
element an intermediate transfer roller which is coated with a silicone or
fluorosilicone elastomer composition, which is heated to between 80-100°C, and
which applies a force of approximately 40-80 lb$_f$ across the entire contact zone with
the photoreceptor. One suitable coating composition for the transfer roller is the Dow
Corning 94-003 fluorosilicone elastomer heated to between 85-95°C. Preferred
28   elastomeric coating compositions are disclosed in U.S. 5,965,314.

The substrate for receiving the image from either the photoreceptive element
in electrophotographic printing or the dielectric element in electrostatic printing can
be any commonly used receptor material, such as paper, coated paper, polymeric
films and primed or coated polymeric films, particularly adhesive coated polymeric

films. Suitable polymeric films include polyesters, plasticized and compounded polyvinyl chloride (PVC), acrylics, polyurethanes, polyethylene/acrylic acid copolymers, (e.g., that available under the trade designation SURLYN and polyvinyl butyrals. Commercially available composite materials such as those having the trade designations SCOTCHCAL, SCOTCHLITE, and PANAFLEX are also suitable for preparing substrates.

7   The transfer of the formed image from the surface of photoreceptor or dielectric element to the final receptor or transfer medium may be enhanced by the incorporation of a release-promoting material within the dispersed particles used to form the image. The incorporation of a silicone-containing material or a fluorine-containing material in the outer (shell) layer of the particle facilitates the efficient transfer of the image.

           In multicolor electrographic imaging, the toners may be applied to the surface
14   of the dielectric element or photoreceptive element in any order, but for colorimetric reasons, bearing in mind the inversion that occurs on transfer, it is sometimes preferred to apply the images in a specified order depending upon the transparency and intensity of the colors. A preferred order for direct imaging or double transfer process is yellow, magenta, cyan and black; for a single transfer process, the preferred order is black, cyan, magenta, and yellow. Yellow is generally imaged first to avoid contamination from other toners and black is generally imaged last due to the black
21   toner acting as a filter of the radiation source.

           Overcoating of the transferred image may optionally be carried out to protect the image from physical damage and/or actinic damage. Compositions for overcoatings are well-known in the art and typically comprise a clear film-forming polymer dissolved or suspended in a volatile solvent. An ultraviolet light absorbing agent may optionally be added to the coating composition. Lamination of protective layers to the image-bearing surface is also well known in the art and may be used.

28   In order to function most effectively, liquid toners preferably have conductance values in the range of 50 to 1200 picomho-cm^{-1} at their working concentrations. Liquid toners prepared according to the present invention preferably have conductance values of from 50 to 500 picomho-cm^{-1} for a dispersion containing

3% by weight solids. Toners are usually prepared in a concentrated form to conserve storage space and reduce transportation costs. In order to use the toners in the printer, the concentrate is diluted with additional carrier liquid to give what is termed the working strength liquid toner.

The crosslinked gel organosol provides an efficient method for formulating a high solids ink. The crosslinked gel organosol will phase separate into two phases, one phase comprising primarily a portion of the carrier liquid and the other phase a concentrated gel organosol dispersion. Once separated, the gel organosol can be simply redispersed with mixing or by removal of the separated carrier liquid form a concentrate of the dispersion. A high solids ink for printing or replenishment may be produced by allowing the organosol to gel and then decanting or siphoning off the supernatant liquid, thus forming a concentrate of the gel polymer in the dispersant liquid. A variety of alternative methods for concentrating the organosol or ink are well known in the art, such as gravity settling, centrifugation, filtration, controlled flocculation, etc. The carrier liquid may be removed either prior to or after the addition of the pigment and/or charge director and either before or after milling the toner.

These and other aspects of the present invention are demonstrated in the illustrative examples that follow.

EXAMPLES

Glossary of Chemical Abbreviations & Chemical Sources

The following raw materials were used to prepare the polymers in the examples which follow:

The catalysts used in the examples are Azobisisobutyronitrile (designated as AIBN, VAZO-64 available from DuPont Chemicals, Wilmington, DE); and Dibutyl Tin Dilaurate (designated as DBTDL, available from Aldrich Chemical Co., Milwaukee, WI). The monomers are all available from Scientific Polymer Products, Inc., Ontario, NY unless designated otherwise.

The monomers used in the examples are designated by the following abbreviations: Dimethyl-m-isopr penyl benzylisocyanate (TMI, available from CYTEC Industries, West Paterson, NJ); Divinyl Benzene (DVB); Ethylene Glycol Dimethacrylate (EGDMA); Ethyl Acrylate (EA); 2-Ethylhexyl Methacrylate (EHMA); 2-Hydroxyethyl Methacrylate (HEMA; Lauryl Methacrylate or Dodecyl Methacrylate (LMA); Methyl Methacrylate (MMA); Octadecyl Acrylate or Stearyl
7   Acrylate (ODA); 1,4 Phenylene Diisocyanate (PDI) and Trimethylolpropane Trimethacrylate (TTMA).

Analytical Test Methods

The following test methods were used to characterize the polymers and inks in the examples that follow:

Percent Solids of Graft Stabilizer, Organosol, and Liquid Toner

Percent solids of the graft stabilizer solutions, and the organosol and ink
14   dispersions, were determined gravimetrically using a halogen lamp drying oven attachment to a precision analytical balance (Mettler Instruments Inc., Hightstown, NJ). Approximately two grams of sample were used in each determination of percent solids using this sample drydown method.

Graft Stabilizer Molecular Weight

Various properties of the graft stabilizer have been determined to be important to the performance of the stabilizer, including molecular weight and molecular weight
21   polydispersity. Graft stabilizer molecular weight is normally expressed in terms of the weight average molecular weight (M_w), while molecular weight polydispersity is given by the ratio of the weight average molecular weight to the number average molecular weight (M_w/M_n). Molecular weight parameters were determined for graft stabilizers with gel permeation chromatography (GPC) using tetrahydrofuran as the carrier solvent. Absolute M_w was determined using a Dawn DSP-F light scattering detector (Wyatt Technology Corp, Santa Barbara,CA), while polydispersity was
28   evaluated by ratioing the measured M_w to a value of M_n determined with an Optilab 903 differential refractometer detector (Wyatt Technology Corp, Santa Barbara, CA).

Organosol Particle Size

       Organosol particle size was determined by dynamic light scattering on a diluted toner sample (typically < 0.0001 g/ml) using a Malvern Zetasizer III Photon Correlation Spectrometer (Malvern Instruments Inc, Southborough, MA). The dilute samples were ultrasonicated for one minute at 100 watts and 20 kiloHz (kHz) prior to measurement. Dynamic light scattering provides a fast method of determining the

7   particle translational diffusion coefficient, which can be related to the z-average particle diameter without detailed knowledge of the optical and physical properties (i.e. refractive index, density and viscosity) of the organosol. Details of the method are described in Chu (Chu, B., Laser Scattering Academic Press, NY 1974, 11A). Since the organosols are comprised of nearly monodisperse, uniform spherical particles, dynamic light scattering provides an absolute measure of particle size for particles having diameters between 25-2500 nm.

14   Liquid Toner Properties

       The characterization of a liquid toner requires the measurement of a number of physical and chemical properties of the toner, as well as direct evaluation of image quality obtained by developing the toner in a LEP imaging mechanism. The measured toner characteristics can be roughly broken down into size-related properties (particle size), charge-related properties (bulk and free phase conductivity, dynamic mobility and zeta potential, and charge/developed reflectance optical density

21   (Q/ROD), a parameter which is directly proportional to the toner charge/mass.

Particle Size

       Toner particle size distributions were determined using a Horiba LA-900 laser diffraction particle size analyzer (Horiba Instruments, Inc, Irvine, CA). Toner samples were diluted approximately 1/500 by volume and sonicated for one minute at 150 watts and 20 kHz prior to measurement. Toner particle size was expressed on a number-average basis in order to provide an indication of the fundamental (primary)

28   particle size of the ink particles.

Toner Conductivity

       The liquid toner conductivity (bulk conductivity, k_b) was determined at approximately 18 Hz using a Scientifica model 627 conductivity meter (Scientifica

Instruments, Inc., Princeton, NJ). In additi n, the free (dispersant) phase conductivity (k_f) in the absence of toner particles was also determined. Toner particles were removed from the liquid milieu by centrifugation at 5°C for 1-2 hours at 6,000 rpm (6,110 relative centrifugal force) in a Jouan MR1822 centrifuge (Winchester, VA). The supernatant liquid was then carefully decanted, and the conductivity of this liquid was measured using a Scientifica Model 627 conductance meter. The percentage of free phase conductivity relative to the bulk toner conductivity was then determined as: 100% (k_f/k_b).

Particle Mobility

Toner particle electrophoretic mobility (dynamic mobility) was measured using a Matec MBS-8000 Electrokinetic Sonic Amplitude Analyzer (Matec Applied Sciences, Inc., Hopkinton, MA). Unlike electrokinetic measurements based upon microelectrophoresis, the MBS-8000 instrument has the advantage of requiring no dilution of the toner sample in order to obtain the mobility value. Thus, it was possible to measure toner particle dynamic mobility at solids concentrations actually preferred in printing. The MBS-8000 measures the response of charged particles to high frequency (1.2 MHz) alternating (AC) electric fields. In a high frequency AC electric field, the relative motion between charged toner particles and the surrounding dispersion medium (including counter-ions) generates an ultrasonic wave at the same frequency of the applied electric field. The amplitude of this ultrasonic wave at 1.2 MHz can be measured using a piezoelectric quartz transducer; this electrokinetic sonic amplitude (ESA) is directly proportional to the low field AC electrophoretic mobility of the particles. The particle zeta potential can then be computed by the instrument from the measured dynamic mobility and the known toner particle size, dispersant liquid viscosity, and liquid dielectric constant.

Particle Charge

Toner charge/mass is an important, albeit difficult to determine parameter useful in predicting the development characteristics (e.g. optical density, overtoning uniformity) for liquid toners. The difficult in determining charge/mass for liquid toners arises from the low developed toner mass (typically 50-200 micro grams/cm^2) associated with the desired developed optical densities (typically > 1.2 reflectance

optical density units). A related parameter which is directly proportional to toner charge/mass is the toner charge/developed optical density. This parameter was determined by plating ink particles in distinct bands covering a range of known plating potentials onto a dielectric sheet coated with a silicone release layer while simultaneously monitoring the total current flow with a sensitive electrometer. The resulting plated toner layer was then air dried and transferred using an offset transfer

7 process to plain paper. The reflectance optical density of the completely transferred toner film on paper was determined using a Greteg SPM50 reflectance optical densitometer (Greteg Instruments Inc., Regensdorf, Sitzerland). The ratio of the total current to the product of the plated toner area and the developed optical density yields the charge/ROD value for that toner, i.e. Charge/ROD = (Total Current)/[(Plated Area)(Reflectance Optical Density)].

Graft Stabilizers

14 In the following examples of graft stabilizer preparations, it will be convenient to summarize the compositional details of each particular graft stabilizer or graft stabilizer precursor by ratioing the weight percentage of monomers employed in the synthesis. For example, a graft stabilizer designated LMA/HEMA-TMI (96/1/3–4.7 %w/w) is made from a graft stabilizer precursor which is a copolymer consisting of 96% weight percent LMA and 3% weight percent HEMA, to which is covalently bonded a grafting site consisting of 4.7 weight percent TMI based on the total weight

21 of the graft stabilizer precursor.

Example 1

This example illustrates the use of a bi-functional crosslinker, divinyl benzene (DVB) containing free radically polymerizable divinyl functionality, to prepare cross linked graft stabilizers. 8 ounce (0.24 liter), narrow mouthed glass bottles were charged with 74.54 g of NORPAR 12, X g of LMA, Y g of DVB (X and Y are listed in Table I), 0.78 g of 96% HEMA and 0.188 g of AIBN. The bottles were purged for

28 two minutes with dry nitrogen at a rate of 1.5 liters/minute, then sealed with a screw cap fitted with a teflon liner. The caps were secured in place using electrical tape. The sealed bottles were then inserted into a metal cage assembly of an Atlas Launder-Ometer (Atlas Electric Devices Company, Chicago, IL). The Launder-Ometer was

operated at a fixed agitation speed of 42 rpm with a water bath temperature of 70°C. The mixtures were allowed to react for 16 hours at 70°C and then cooled to room temperature. The conversion in each case was quantitative.

The products are crosslinked copolymers of LMA and HEMA and are designated herein as LMA/DVB/HEMA. Determination of the molecular weight was made using the GPC method described previously for LMA/DVB/HEMA

7   (96.5/0.5/3); M_w of 412,585 Da and M_w/M_n of 7.32, and LMA/DVB/HEMA (96.4/0.6/3); M_w of 418,742 Da and M_w/M_n of 7.34. Molecular weight determinations of graft stabilizer precursors with more than 0.6% DVB were not possible as the polymers were highly crosslinked and therefore insoluble in the carrier solvent employed for GPC molecular weight analysis.

From Table 2 it can be seen that the maximum amount of DVB tolerated in this system is less than 1 % w/w before the onset of solidification.

14   **Table 2 - Summary of reaction data for Example 1**

Graft stabilizer precursor ID, (LMA/DVB/HEMA)	DVB (% w/w)	DVB Y (g)	LMA X(g)	Appearance after 16hrs at 70°C
96.5/0.5/3	0.5	0.125	24.37	Clear colorless viscous solution
96.4/0.6/3	0.6	0.15	24.34	Clear colorless viscous solution
96.25/0.75/3	0.75	0.189	24.31	Clear colorless extremely viscous solution
96.1/0.9/3	0.9	0.227	24.27	Semi solid gel with some mobility
96/1/3	1.0	0.253	24.24	solid gel with very little mobility
95.5/1.5/3	1.5	0.379	24.12	solid 'rubber like' material

<u>Example 2</u>

A 3000 mL 3-necked round bottom flask equipped with an overhead mechanical stirrer, condenser, a thermocouple connected to a digital temperature controller, and a nitrogen inlet tube connected to a source of dry nitrogen was charged

with a mixture of 1386.5 g NORPAR 12, 463 g of LMA, 2.4 g of DVB, 14.8 g of 96% HEMA and 3.56 g of AIBN. While mechanically stirring, the reaction flask was purged with dry nitrogen for 30 minutes at a flow rate of approximately 2 liters/minute. The nitrogen flow rate was then adjusted to approximately 0.5 liters/min. The mixture was heated to 70°C with stirring, and allowed to polymerize at 70°C for 16 hours. The conversion was quantitative.

7   The mixture was heated to 90°C and held at that temperature for 1 hour to destroy any residual AIBN, then cooled back to 70°C. The nitrogen inlet tube was then removed, and 7.37 g of 95% DBTDL were added to the mixture, followed by 22.33 g of TMI. The TMI was added dropwise over the course of approximately 5 minutes while stirring the reaction mixture. The nitrogen inlet tube was replaced and the flow rate adjusted to 0.5 liters/min and the mixture allowed to react for 6 hours at 70°C and then cooled to room temperature. The conversion in each case was

14   quantitative.

The cooled mixture was a viscous transparent solution containing no visible insoluble material. The percent solids of the mixture was determined to be 26.3% using the halogen drying method described previously. Subsequent determination of the molecular weight was made using the GPC method described previously; the crosslinked copolymer had a M_w of 414,635 Da and a M_w/M_n of 7.34. The product is a crosslinked copolymer of LMA and HEMA containing random side chains of TMI

21   and is designated herein as LMA/DVB/HEMA-TMI (96.5/0.5/3–4.7 w/w%).

Example 3

Using the method and apparatus of Example 1, 73.52 g of NORPAR 12, X g of 95% ODA, Y g of DVB (X and Y are listed in Table 2), 0.78 g of 96% HEMA and 0.188 g of AIBN were combined in the glass bottles, purged with nitrogen, and the resulting mixtures heated at 70°C for 16 hours, after which time the bottles were opened and 1.18 g of TMI and 0.39 g of DBTDL added. The bottles were then

28   purged for two minutes with dry nitrogen at a rate of 1.5 liters/minute, then sealed with a screw cap fitted with a teflon liner. The caps were secured in place using electrical tape. The sealed bottles were then inserted into a metal cage assembly of an Atlas Launder-Ometer (Atlas Electric Devices Company, Chicago, IL). The Launder-

Ometer was operated at a fixed agitati n speed of 42 rpm with a water bath temperature of 70°C. The mixtures were allowed to react for 6 hours at 70°C and then cooled to room temperature. The conversion in each case was quantitative.

The products are crosslinked copolymers of ODA and HEMA containing random side chains of TMI and are designated herein as ODA/DVB/HEMA-TMI. Determination of the molecular weight was made using the GPC method described previously for ODA/DVB/HEMA-TMI (96.5/0.5/3-4.7); M_w of 439,110 Da and M_w/M_n of 6.81. Molecular weight determinations of graft stabilizer precursors with more than 0.5% DVB were not possible as the polymers were highly crosslinked and therefore insoluble in the carrier solvent employed for GPC molecular weight analysis.

From Table 3 it can be seen that the maximum amount of DVB tolerated in this system is less than 1 % w/w before the onset of solidification.

Table 3 - Summary of reaction data for Example 3

Graft stabilizer precursor ID, (ODA/DVB/HEMA-TMI)	DVB (% w/w)	DVB Y (g)	ODA X(g)	Appearance
96.5/0.5/3-4.7	0.5	0.125	25.39	Clear colorless viscous solution
96/1/3-4.7	1.0	0.253	25.26	solid gel with very little mobility
95.5/1.5/3-4.7	1.5	0.379	24.12	solid 'rubber like' material

<u>Example 4</u>

Using the method and apparatus of Example 3, 110 g of NORPAR 12, 36 g of EHMA, X g of DVB (X = 0.09, 0.19, 0.28 and 0.38 g corresponding to 0.25, 0.5, 0.75 and 1 weight percent respectively), 0.68 g of 96% HEMA, and 0.27 g of AIBN were combined in the glass bottles, purged with nitrogen, and the resulting mixtures heated at 70°C for 16 hours, after which time the bottles were opened and 1.8 g of TMI and 0.6 g of DBTDL added. The mixtures were then allowed to react for 6 hours at 70°C and then cooled to room temperature. The conversion in each case was quantitative.

The products are crosslinked copolymers of EHMA and HEMA containing random side chains of TMI and are designated herein as EHMA/DVB/HEMA-TMI. Determination of the molecular weight was made using the GPC method described previously for EHMA/DVB/HEMA-TMI (96.75/0.25/3-4); M_w of 340,098,110 Da and M_w/M_n of 8.79. Molecular weight determinations of graft stabilizer precursors with more than 0.25% DVB were not possible as the polymers were highly crosslinked and therefore insoluble in the carrier solvent employed for GPC molecular weight determination.

From Table 4 it can be seen that the maximum amount of DVB tolerated in this system is approximately 0.5 % w/w before the onset of solidification.

Table 4 - Summary of reaction data for Example 4

Graft stabilizer ID, (EHMA/DVB/HEMA-TMI)	DVB (% w/w)	Appearance
96.75/0.25/3-4.7	0.25	Clear colorless viscous solution
96.5/0.5/3-4.7	0.5	Clear colorless extremely viscous solution
96.25/0.75/3-4.7	0.75	solid gel with very little mobility
96/1/3-4.7	1.0	solid 'rubber like' material

<u>Example 5</u>

This example illustrates the use of a bifunctional crosslinker, ethylene glycol dimethacrylate (EGDMA) containing free radically polymerizable dimethacryate functionality, to prepare crosslinked graft stabilizers. Using the method and apparatus of Example 3, 93.2 g of NORPAR 12, X g of LMA (X = 30.54, 30.46, 30.38, 30.3 and 30.14 g respectively), Y g of EGDMA (Y = 0.08, 0.16, 0.24, 0.32 g and 0.48 g corresponding to 0.25, 0.5, 0.75, 1 and 1.5 weight percent respectively), 0.98 g of 96% HEMA, and 0.23 g of AIBN were combined in the glass bottles, purged with nitrogen, and the resulting mixtures heated at 70°C for 16 hours, after which time the bottles were opened, 1.47 g of TMI and 0.485 g of DBTDL were added, and the

mixtures were allowed to react for 6 h urs at 70°C and then cooled t room temperature. The conversion in each case was quantitative.

The products are crosslinked copolymers of LMA and HEMA containing random side chains of TMI and are designated herein as LMA/EGDMA/HEMA-TMI. Determination of the molecular weight was made using the GPC method described previously for LMA/EGDMA/HEMA-TMI (96/1/3-4.7); M_w of 391,625 Da and

7   M_w/M_n of 8.86. Molecular weight determinations of graft stabilizer precursors with more than 1.0% EGDMA were not possible as the polymers were highly crosslinked and therefore insoluble in the carrier solvent employed for GPC molecular weight determination.

From Table 5 it can be seen that the maximum level of EGDMA tolerated in this system is less than 1.5 % w/w before the onset of solidification.

14   **Table 5 - Summary of reaction data for Example 5**

Graft stabilizer ID, (LMA/EGDMA/HEMA-TMI)	EGDMA (% w/w)	Appearance after 16hrs at 70°C
96.75/0.25/3-4.7	0.25	Clear colorless viscous solution
96.5/0.5/3-4.7	0.5	Clear colorless viscous solution
96.25/0.75/3-4.7	0.75	Clear colorless viscous solution
96/1/3-4.7	1.0	Clear colorless very viscous solution
95.5/1.5/3-4.7	1.5	Semi-solid gel with very little mobility

Example 6

This example illustrates the use of a tri-functional crosslinker, trimethylolpropane trimethacrylate (TTMA) containing free radically polymerizable triacrylate functionality, to prepare crosslinked graft stabilizers. Using the method and apparatus of Example 3, 93.2 g of NORPAR 12, X g of LMA (X = 30.49, 30.37, 30.24 and 30.11 g respectively), Y g of TTMA (X = 0.13, 0.25, 0.39 and 0.51 g

corresponding to 0.4, 0.8, 1.2 and 1.6 weight percent respectively), 0.98 g f 96%

HEMA, and 0.23 g of AIBN were combined in the glass bottles, purged with nitrogen,

and the resulting mixtures heated at 70°C for 16 hours, after which time the bottles

were opened and 1.47 g of TMI and 0.485 g of DBTDL added. The mixtures were

then allowed to react for 6 hours at 70°C and then cooled to room temperature. The

conversion in each case was quantitative.

7   The products are crosslinked copolymers of LMA and HEMA containing

random side chains of TMI and are designated herein as LMA/TTMA/HEMA-TMI.

Determination of the molecular weight was made using the GPC method described

previously for LMA/TTMA/HEMA-TMI (95.8/1.2/3-4.7); M_w of 445,847 Da and

M_w/M_n of 7.45.

From Table 6 it can be seen that the maximum level of TTMA tolerated in this

system is less than 1.6 % w/w before the onset of solidification.

14   **Table 6 - Summary of reaction data for Example 6**

Graft stabilizer ID, (LMA/TTMA/HEMA-TMI)	TTMA (% w/w)	Appearance
96.6/0.4/3-4.7	0.4	Clear colorless viscous solution
96.2/0.8/3-4.7	0.8	Clear colorless viscous solution
95.8/1.2/3-4.7	1.2	Clear colorless very viscous solution
95.6/1.6/3-4.7	1.6	Semi-solid gel with very little mobility

Example 7

This example illustrates the use of a bifunctional crosslinker, 1,4 phenylene

diisocyanate (PDI) containing diisocyanate functionality, that can be readily reacted

with excess hydroxyl groups from the HEMA component of the graft stabilizer (3%

excess) to prepare crosslinked graft stabilizers. Using the method and apparatus of

Example 3, 72.8 g of NORPAR 12, X g of LMA (X = 24.48 and 24.36 g

respectively), 1.56 g of 96% HEMA and 0.23 g of AIBN were combined in the glass bottles, purged with nitrogen, and the resulting mixtures heated at 70°C.

After 16 hours, the bottles were opened and Y g of PDI (Y = 0.253 and 0.379 g corresponding to 1.0 and 1.5 weight percent respectively), 1.18 g of TMI, and 0.39 g of DBTDL were added and the mixtures allowed to react for 6 hours at 70°C and then cooled to room temperature. The conversion in each case was quantitative.

7   The products are crosslinked copolymers of LMA and HEMA containing random side chains of TMI and crosslinks through the ungrafted excess hydroxyl functionality of the HEMA and are designated herein as LMA/PDI/HEMA-TMI. Determination of the molecular weight was made using the GPC method described previously for LMA/PDI/HEMA-TMI (93/1/6–4.7); M_w of 385,041 Da and M_w/M_n of 7.74.

From Table 7 it can be seen that the maximum level of PDI tolerated in this 14   system is less than 1.5 % w/w before the onset of solidification.

Table 7 - Summary of reaction data for Example 7

Graft stabilizer ID, (LMA/PDI/HEMA-TMI)	PDI (% w/w)	Appearance
93/1/6–4.7	1.0	Clear straw colored viscous solution
92.5/1.5/6–4.7	1.5	Semi-solid gel with very little mobility

Example 8

This is an example of a crosslinked graft stabilizer which can be used to produce a gel organosol in a solvent having a solubility parameter lower than that of NORPAR 12. Using the method and apparatus of Example 3, 149.1 g of NORPAR 13, 48.7 g of LMA, 0.25 g of DVB, 1.56 g of 96% HEMA, and 0.23 g of AIBN were 21   combined in a glass bottle, purged with nitrogen, and the resulting mixture heated at 70°C for 16 hours, after which time the bottle was opened and 2.35 g of TMI and 0.78

g of DBTDL were added. The mixtures were allowed to react for 6 hours at 70°C and then cooled to room temperature. The conversion in each case was quantitative.

The product is a crosslinked copolymer of LMA and HEMA containing random side chains of TMI and is designated herein as LMA/DVB/HEMA-TMI. Determination of the molecular weight was made using the GPC method described previously for LMA/DVB/HEMA-TMI (96.5/0.5/3-4.7); M_w of 455,141 Da and

7   M_w/M_n of 6.81.

Organosol Examples

In the following examples of organosol preparation, it will be convenient to summarize the composition of each particular organosol in terms of the ratio of the total weight of monomers comprising the organosol core relative to the total weight of monomers comprising the organosol shell. The ratio is referred to as the core/shell ratio of the organosol. In addition, it will be useful to summarize the compositional

14   details of each particular organosol by ratioing the weight percentages of monomers used to create the shell and the core, for example, an organosol designated LMA/DVB/HEMA-TMI//MMA/EA (96.5/0.5/3-4.7//25/75 % w/w) is made form shell comprised of graft stabilizer precursor which is a crosslinked copolymer consisting of 96.5 weight percent of LMA, 0.5 weight percent of DVB and 3 weight percent of HEMA, to which is covalently bonded a grafting site consisting of 4.7 weight percent of TMI bases on the total weight of graft stabilizer precursor. The

21   graft stabilizer is covalently bonded to a core that is comprised of 25 weight percent MMA and 75 weight percent of EA.

Example 9

This example illustrates the use of the graft stabilizer in Example 2 to prepare a gel organosol with a core/shell ratio of 8/1. A 3000 mL 3-necked round bottom flask equipped with an overhead mechanical stirrer, condenser, a thermocouple connected to a digital temperature controller, and a nitrogen inlet tube connected to a

28   source of dry nitrogen was charged with a mixture of 1597.6 g of NORPAR 12, 96.3 g of the graft stabilizer from Example 2 at 26.3% solids, 50.7 g of MMA, 152 g of EA, and 3.42 g of AIBN. While mechanically stirring, the reaction flask was purged

44

with dry nitrogen for 30 minutes at a flow rate of approximately 2 liters/minute. The nitrogen flow rate was then adjusted to approximately 0.5 liters/min. The mixture was heated to 70°C with stirring, and allowed to polymerize at 70°C for 16 hours, at which time the organosol was cooled to room temperature.

Approximately 180 g of n-heptane were added to the cooled organosol and the resulting mixture was stripped of residual monomer using a rotary evaporator

7   equipped with a dry ice/acetone condenser and operating at a temperature of 95°C, and reducing the vacuum gradually so as to maintain an adequate condensate collection rate to approximately 15 mm Hg. The stripped organosol was cooled to room temperature, yielding an opaque white dispersion which formed a gel over a period of a two hours.

This gel organosol is designated LMA/DVB/HEMA-TMI//MMA/EA (96.5/0.5/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent

14   solids of this organosol was determined as 15.7% using the halogen drying method outlined above. A satisfactory determination of the particle size of the organosol using the light scattering method described previously was not possible owing to settling of the particles during the time scale of the experiment.

Example 10

This example illustrates the use of the graft stabilizer in Example 3, ODA/DVB/HEMA-TMI (96.5/0.5/3-4.7), to prepare a gel organosol with a core/shell

21   ratio of 8/1. An 8 ounce (0.24 liter), narrow mouthed glass bottle was charged with 84.1 g of NORPAR 12, 8.1 g of EA, 2.69 g of MMA, 4.94 g of the graft stabilizer from Example 3 at 27.0% solids, and 0.18 g of AIBN. The bottle was purged for two minutes with dry nitrogen at a rate of 1.5 liters/minute, then sealed with a screw cap fitted with a teflon liner. The cap was secured in place using electrical tape. The sealed bottle was then inserted into a metal cage assembly of an Atlas Launder-Ometer (Atlas Electric Devices Company, Chicago, IL). The Launder-Ometer was

28   operated at a fixed agitation speed of 42 rpm with a water bath temperature of 70°C. The mixture was allowed to react for 16 hours at 70°C, at which time the organosol was cooled to room temperature yielding an opaque white dispersion that formed a gel over 3 hours.

This gel organ sol is designated ODA/DVB/HEMA-TMI//MMA/EA (96.5/0.5/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent solids of this organosol was determined as 11.6% using the halogen drying method outlined above. Subsequent determination of average particle size was made using the dynamic light scattering method described above; the organosol had a z-average diameter of 229 nm.

7

Example 11

This example illustrates the use of the graft stabilizer in Example 4, EHMA/DVB/HEMA-TMI (96.75/0.25/3-4.7), to prepare a gel organosol with a core/shell ratio of 8/1. A 16 ounce (0.48 liter), narrow mouthed glass bottle was charged with 251.5 g of NORPAR 12, 24.0 g of EA, 8.0 g of MMA, 15.99 g of the graft stabilizer from Example 4 at 25.0% solids, and 0.54 g of AIBN. The bottle was purged for two minutes with dry nitrogen at a rate of 1.5 liters/minute, then sealed

14   with a screw cap fitted with a teflon liner. The cap was secured in place using electrical tape. The sealed bottle was then inserted into a metal cage assembly of an Atlas Launder-Ometer (Atlas Electric Devices Company, Chicago, IL). The Launder-Ometer was operated at a fixed agitation speed of 42 rpm with a water bath temperature of 70°C. The mixture was allowed to react for 16 hours at 70°C, at which time the organosol was cooled to room temperature yielding an opaque white dispersion that formed a strong gel within 1 hour.

21   This gel organosol is designated EHMA/DVB/HEMA-TMI//MMA/EA (96.75/0.25/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent solids of this organosol was determined as 11.8% using the halogen drying method outlined above. Subsequent determination of average particle size was made using the dynamic light scattering method described above; the organosol had a z-average diameter of 562 nm.

Example 12

28   This example illustrates the use of the graft stabilizer in Example 5, LMA/EGDMA/HEMA-TMI (96/1/3-4.7), to prepare a gel organosol with a core/shell ratio of 8/1. Using the method and apparatus of Example 11, 251.8 g of NORPAR 12,

24.0 g of EA, 8.0 g of MMA, 5.2 g of the graft stabilizer solution from Example 5 at

25.5% solids, and 0.54 g f AIBN were combined in a reaction bottle and the

resulting mixture reacted at 70°C for 16 hours, at which time the organosol was

cooled to room temperature, yielding an opaque white dispersion that formed a gel

within 1 hour.

This gel organosol is designated LMA/EGDMA/HEMA-TMI//MMA/EA

7   (96/1/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent solids of

this organosol was determined as 12.0% using the halogen drying method outlined

above. Subsequent determination of average particle size was made using the

dynamic light scattering method described above; the organosol had a z-average

diameter of 474 nm using the halogen drying method outlined above.

Example 13

This example illustrates the use of the graft stabilizer in Example 6,

14   LMA/TTMA/HEMA-TMI (95.8/1.2/3-4.7), to prepare a gel organosol with a

core/shell ratio of 8/1. Using the method and apparatus of Example 10, 83.9 g of

NORPAR 12, 8.08 g of EA, 2.69 g of MMA, 5.19 g of the graft stabilizer solution

from Example 6 at 25.7% solids, and 0.18 g of AIBN were combined in a reaction

bottle and the resulting mixture reacted at 70°C for 16 hours, at which time the

organosol was cooled to room temperature, yielding an opaque white dispersion that

formed a gel over 3 hours.

21   This gel organosol is designated LMA/TTMA/HEMA-TMI//MMA/EA

(95.8/1.2/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent

solids of this organosol was determined as 11.5% using the halogen drying method

outlined above. A satisfactory determination of the particle size of the organosol using

the light scattering method described previously was not possible owing to settling of

the particles during the time scale of the experiment.

Example 14

28   This example illustrates the use of the graft stabilizer in Example 7,

LMA/PDI/HEMA-TMI (96/1/3-4.7), to prepare a gel organosol with a core/shell ratio

of 8/1. Using the method and apparatus of Example 10, 83.9 g of NORPAR 12, 8.08

g of EA, 2.69 g of MMA, 5.13 g of the graft stabilizer solution from Example 7 at 26.0% solids, and 0.18 g of AIBN were combined in a reaction bottle and the resulting mixture reacted at 70°C for 16 hours, at which time the organosol was cooled to room temperature yielding, an opaque white dispersion that formed a gel over 1 hour.

7   This gel organosol is designated LMA/PDI/HEMA-TMI//MMA/EA (96/1/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent solids of this organosol was determined as 11.5% using the halogen drying method outlined above. A satisfactory determination of the particle size of the organosol using the light scattering method described previously was not possible owing to settling of the particles during the time scale of the experiment.

Example 15

14   This example illustrates the use of the graft stabilizer in Example 8 to prepare a gel organosol with a core/shell ratio of 8/1 in a solvent having a Hildebrand solubility parameter lower than that of NORPAR 12. Using the method and apparatus of Example 10, 83.9 g of NORPAR 13, 8.08 g of EA, 2.69 g of MMA, 5.15 g of the graft stabilizer solution from Example 8 at 25.9% solids, and 0.18 g of AIBN were combined in a reaction bottle and the resulting mixture reacted at 70°C for 16 hours, at which time the organosol was cooled to room temperature, yielding an opaque white dispersion that formed a weak gel over 24 hours.

21   This gel organosol is designated LMA/DVB/HEMA-TMI//MMA/EA (96.5/0.5/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent solids of this organosol was determined as 11.6% using the halogen drying method outlined above. Subsequent determination of average particle size was made using the dynamic light scattering method described above; the organosol had a z-average diameter of 312 nm.

Example 16

28   This example illustrates the use of the graft stabilizer in Example 2 to prepare a gel organosol with a core/shell ratio of 4/1. Using the method and apparatus of Example 11, 162.0 g of NORPAR 12, 14.55 g of EA, 4.85 g of MMA, 18.25 g of the

graft stabilizer soluti n from Example 2 at 26.3% solids, and 0.36 g f AIBN were combined in a reaction bottle and the resulting mixture reacted at 70°C for 16 hours, at which time the organosol was cooled to room temperature, yielding an opaque white dispersion that formed a weak gel over 24 hours.

This gel organosol is designated LMA/PDI/HEMA-TMI//MMA/EA (96/1/3-4.7//25/75 % w/w) having a calculated T_g equal to -1°C. The percent solids of this organosol was determined as 11.7% using the halogen drying method outlined above. A satisfactory determination of the particle size of the organosol using the light scattering method described previously was not possible owing to settling of the particles during the time scale of the experiment.

Liquid Toner Examples

Example 17

This is an example of preparing a cyan liquid toner at an organosol/pigment ratio of 8 using the gel organosol prepared in Example 9 at core/shell ratio of 8. The organosol of Example 9 was mixed using a Silverson mixer (Model L22R, Silverson machines. Ltd, Waterside, England) operated at the lowest speed setting. After mixing for 5 minutes, 203.8 g of the homogenized organosol at 15.7% (w/w) solids in NORPAR 12 were combined with 88.3 g of NORPAR 12, 4 g of Pigment Heliogen Blue L7560 (BASF), and 3.90 g of 6.16% Zirconium HEX-CEM solution (OMG chemical company, Cleveland, Ohio) in an eight ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Aimex Co.,Ltd., Tokyo, Japan) charged with 390 g of 1.3mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2000 rpm for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

A portion of this 12% (w/w) solids toner concentrate was diluted to approximately 3% (w/w). This dilute toner sample exhibited the following properties as determined using the test methods described above:

Number Mean Particle Size: 1.00 micron

Bulk Conductivity: 75 picoMhos/cm

Percent Free Phase Conductivity: 4%

Dynamic M bility: 0.0367 micron-cm/[Volt-second]

Zeta Potential: 75 mV

This working strength toner was tested on the plating apparatus described previously. The reflection optical density (ROD) was greater than 1.2 at plating voltages greater than 450 volts.

Example 18

7

This is an example of preparing a yellow liquid toner at an organosol/pigment ratio of 6 using the gel organosol prepared in Example 9 at core/shell ratio of 8. The organosol of Example 9 was mixed using a Silverson mixer (Model L22R, Silverson machines. Ltd, Waterside, England) operated at the lowest speed setting. After mixing for 5 minutes, 196.5 g of the homogenized organosol at 15.7% (w/w) solids in NORPAR 12 were combined with 95.8 g of NORPAR 12, 5.14 g of Pigment Yellow

14   83 (C.I. 21108;#275-0570, Sun Chemical Company, Cincinnati, Ohio), and 2.5 g of 6.16% Zirconium HEX-CEM solution (OMG Chemical Company, Cleveland, Ohio) in an eight ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Aimex Co.,Ltd., Tokyo, Japan) charged with 390 g of 1.3mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2000 rpm for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

21   A portion of this 12% (w/w) solids toner concentrate was diluted to approximately 3% (w/w). This dilute toner sample exhibited the following properties as determined using the test methods described above:

Number Mean Particle Size: 0.679 micron

Bulk Conductivity: 205 picoMhos/cm

Percent Free Phase Conductivity: 12%

Dynamic Mobility: 0.0444 micron-cm/[Volt-second]

28   Zeta Potential: 90 mV

This working strength toner was tested on the plating apparatus described previously. The reflection optical density (ROD) was greater than 1.2 at plating voltages greater than 450 volts.

Example 19

This is an example of preparing a magenta liquid toner at an organosol/pigment ratio of 6 using the gel organosol prepared in Example 9 at core/shell ratio of 8. The organosol of Example 9 was mixed using a Silverson mixer (Model L22R, Silverson machines. Ltd, Waterside, England) operated at the lowest speed setting. After mixing for 5 minutes, 196.5 g of the homogenized organosol at

7   15.7% (w/w) solids in NORPAR 12 were combined with 98.1 g of NORPAR 12, 5.14 g of Pigment Red 81 (C.I. 45160;#221-0021, Max Marx Company, Irvington, NJ), and 0.21 g of 6.16% Zirconium HEX-CEM solution (OMG chemical company, Cleveland, Ohio) in an eight ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Aimex Co.,Ltd., Tokyo, Japan) charged with 390 g of 1.3mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2000 rpm for 1.5 hours without cooling

14   water circulating through the cooling jacket of the milling chamber.

A portion of this 12% (w/w) solids toner concentrate was diluted to approximately 3% (w/w). This dilute toner sample exhibited the following properties as determined using the test methods described above:

> Number Mean Particle Size: 0.512 micron
> Bulk Conductivity: 198 picoMhos/cm
> Percent Free Phase Conductivity: 9%

21   Dynamic Mobility: 0.0335 micron-cm/[Volt-second]
> Zeta Potential: 67 mV

This working strength toner was tested on the plating apparatus described previously. The reflection optical density (ROD) was greater than 1.3 at plating voltages greater than 450 volts.

Example 20

This is an example of preparing a black liquid toner at an organosol/pigment

28   ratio of 6 using the gel organosol prepared in Example 9 at core/shell ratio of 8. The organosol of Example 9 was mixed using a Silverson mixer (Model L22R, Silverson machines. Ltd, Waterside, England) operated at the lowest speed setting. After mixing for 5 minutes, 196.5 g of the homogenized organosol at 15.7% (w/w) solids in

NORPAR 12 were combined with 95 g of NORPAR 12, 5.14 g of Monarch 120 carbon black (Cabot Corporation, Billerica, Mass.), and 3.34 g of 6.16% Zirconium HEX-CEM solution (OMG Chemical Company, Cleveland, Ohio) in an eight ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Aimex Co.,Ltd., Tokyo, Japan) charged with 390 g of 1.3mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2000 rpm for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

A portion of this 12% (w/w) solids toner concentrate was diluted to approximately 3% (w/w). This dilute toner sample exhibited the following properties as determined using the test methods described above:

Number Mean Particle Size: 0.241 micron

Bulk Conductivity: 304 picoMhos/cm

Percent Free Phase Conductivity: 5%

Dynamic Mobility: 0.0466 micron-cm/[Volt-second]

Zeta Potential: 93 mV

This working strength toner was tested on the plating apparatus described previously. The reflection optical density (ROD) was greater than 1.2 at plating voltages greater than 450 volts.

<u>Example 21</u>

This example illustrates the preparation of a high solids gel organosol from a preformed lower solids gel organosol. Such high solids organosols can be used to prepare high solids toner concentrates suitable for use as toner replenishments in liquid immersion development.

Approximately 1000 g of the gel organosol mixture of Example 9 at 15.7% solids was stored without agitation in a two liter wide mouth polyethylene bottle. After approximately 24 hours, the sample had separated into a lower gel phase and a clear supernatant liquid phase consisting essentially of NORPAR 12. The clear supernatant liquid was carefully decanted, and a sample of the lower gel phase was removed. The percent solids of this sample of concentrated gel organosol was determined using the infrared drying method described above. The gel organosol

solids had increased from 15.7% to 25.0%. The resulting g l organosol concentrate
can be used to prepare gel inks at concentrations greater than 25% (w/w).

Example 22

This example illustrates the preparation of a high solids gel ink from a
preformed lower solids gel ink. This example also illustrates a method for
additionally reducing the free phase conductivity of such gel ink concentrates relative

7   to the starting ink. Such high solids ink with reduced free phase conductivity are
particularly useful as toner replenishers in liquid immersion development.

Approximately 35 g of the yellow gel ink at 12.0% solids (4.4% free phase
conductivity) from Example 18 was transferred to a 50 mL centrifuge tube and
centrifuged at 5°C. for 5 minutes at 7500 rpm (7,640 relative centrifugal force) in a
Jouan MR1822 centrifuge. The ink separated into a lower pigmented gel phase and a
clear supernatant liquid phase consisting of essentially NORPAR 12. The clear

14   supernatant liquid was carefully decanted, and a sample of the lower gel phase was
removed. The percent solids of this sample of concentrated gel toner was determined
using the infrared drying method described above. The gel toner solids had increased
from 12.0% to 27.0%. Approximately 10 g of NORPAR 12 was added to this gel
toner concentrate. The gel concentrate was mixed by shaking the capped centrifuge
tube. The concentrated gel ink readily redispersed upon mixing with the added
NORPAR 12. This sample was centrifuged at 5°C. for 1 hour at 7500 rpm (7,640

21   relative centrifugal force) in the Jouan MR1822 centrifuge. The supernatant was then
carefully decanted, and the conductivity of this solution was then measured using a
Scientifica Model 627 conductivity meter operating at 12 Hz. The percentage of free
phase conductivity relative to the bulk toner conductivity was now found to be
approximately 0.5%. The resulting ink concentrate of reduced free phase
conductivity is particularly suited for use as a high solids replenisher for liquid
immersion development.

28   A number of embodiments of the invention have been described.
Nevertheless, it will be understood that various modifications may be made without
departing from the spirit and scope of the invention. Accordingly, ther embodiments
are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A gel organosol dispersion comprising:

    (a)   a carrier liquid having a Kauri-Butanol number less than 30; and

    (b)   a covalently crosslinked graft copolymer comprising a copolymeric steric stabilizer covalently bonded to a thermoplastic (co)polymeric core that is insoluble in said carrier liquid,

wherein said steric stabilizer comprises the reaction product of a monomer mixture comprising no greater than 2% by weight of a crosslinking monomer having a functionality of two or more.

2. A gel organosol dispersion according to claim 1 wherein said dispersion further comprises a colorant.

3. A gel organosol dispersion according to any one of the preceding claims wherein said monomer mixture comprises between 0.1 and 2% by weight of said crosslinking monomer.

4. A gel organosol dispersion according to any one of the preceding claims wherein said dispersion has a solids content of at least 2% by weight.

5. A gel organosol dispersion according to any one of the preceding claims wherein said thermoplastic core has a Tg less than 30°C.

6. A gel organosol dispersion according to any one of the preceding claims wherein the ratio of said core to said stabilizer to said core on a weight to weight basis is between 1/1 and 15/1.

7. A gel organosol dispersion according to any one of the preceding claims wherein said crosslinking monomer is from the group consisting of ethylene glycol dimethacrylate, trimethylolpropane trimethylacrylates, and 1,4 phenylene diisocyanate divinyl benzene.

8. A gel organosol dispersion according to claim 2 wherein said colorant comprises a pigment.

54

9.   A gel organosol dispersi n according to claim 8 wherein the ratio f said graft copolymer to said pigment on a weight to weight basis is between 1/1 and 20/1.

10. A gel organosol dispersion according to any one of the preceding claims wherein said dispersion further comprises a charge director.